SUPPLEMENT TO MELLOR'S COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

VOLUME II
SUPPLEMENT II
Li, Na

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

By J. W. Mellor, D.Sc., F.R.S.

Vol. I.	H, O.
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Vol. XII.	U, Mn, Ma, and Re, Fe (Part I).
Vol. XIII.	Fe (Part II).
Vol. XIV.	Fe (Part III), Co.
Vol. XV.	Ni, Ru, Rh, Pd, Os, Ir.
Vol. XVI.	Pt and general index.

SUPPLEMENTS

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	Supp. III.	K, Rb, Cs.

Supplement to

MELLOR'S COMPREHENSIVE
TREATISE ON

INORGANIC AND THEORETICAL CHEMISTRY

Prepared under the direction
of an Editorial Board

VOLUME II

SUPPLEMENT II

The Alkali Metals

Part 1

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PREFACE

The first Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry was devoted to the chemistry of the halogens, and was entitled Supplement 2, Part 1. It now appears that this description did not convey sufficiently clearly the information that it constituted the Supplement to the first part of the original Volume 2. In future, therefore, it will be known as Volume 2, Supplement 1, and the Supplement now presented will be Volume 2, Supplement 2, The Alkali Metals, Part 1, since it deals with lithium and sodium, which with potassium, rubidium and caesium occupy the second part of the original Volume 2.

Once it was realised that the extent of the information on the alkali metals to be discussed would preclude its presentation in a single supplement there seemed little reason to delay, even for a short period, the publication of that relating to lithium and sodium until the whole of the matter relating to the other alkali metals, and to the radiochemistry of the group, could also be placed in the hands of readers. The task of collecting, considering, and presenting the information of importance in the chemistry of the alkali metals which has become available since the original Treatise was published has proved formidable and unexpectedly prolonged. An attempt to survey most of the literature published during the intervening period has, however, been made, as will be evident to readers who notice the frequency with which additional references, enumerated *a*, *b*, etc., have been incorporated.

At an early stage it was recognised that although the various sections of the subject would be written by a large number of different authors according to their individual interests, knowledge, and experience, much of the material to be distributed to, and used by, them was published, abstracted and indexed with reference to the elements as a group. This circumstance, while facilitating comparative studies of the elements concerned, tended at first to clog the 'machine', and was eliminated as a major source of delay only after experience had been painfully gained. Yet another cause of delay was the death of no less than three valued contributors: Mr. F.W. James, Dr. N. Miller and Dr. P.C.L. Thorne, whose loss to the science of chemistry in general, and in particular to the editorial board responsible for the production of this volume, cannot be measured simply by reference to any scientific communications bearing their names as authors, but must take account also of much help of which this expression of thanks can be the only public recognition.

Mellor's convention, that only the hydrides, oxides, halides, sulphides, sulphates, carbonates, nitrates and phosphates of metals should be considered under the general heading of the respective metals, all other salts being discussed under the appropriate non-metallic element of the acid, has again been adopted.

The general plan on which the Supplements to Mellor's Comprehensive Treatise have been conceived and the limitations of their design, with an indication of the considerations on which invitations to contribute are based, together with some description of the mechanism employed in collecting, sifting and presenting an enormous mass of information in the form of a collection of monographs having the same general pattern but individual qualities reflecting the author's judgment, have been set out in the Preface to the Supplement on the halogens. Readers are therefore referred to that Preface if they wish to be reminded of these matters.

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Everyone who has been concerned with the preparation of these Supplements will join in our expression of indebtedness to all those authors, reviewers and abstractors of scientific papers whose meticulous disclosure of experimental observations, theoretical arguments, criticism, or simply presentation of relevant material in a convenient form, supply the essential foundation not merely of a work of the character of Mellor's 'Comprehensive Treatise' but of all scientific advancement. The task of preparing the Supplement devoted to Lithium and Sodium has been materially lightened by the ready collaboration of individual chemists; the Editors have also received valued encouragement and help from industrial and governmental organisations, in particular Imperial Chemical Industries Ltd., Messrs. Johnson Matthey & Co. Ltd., Associated Lead Manufacturers Ltd., The Nitrate Corporation of Chile, and the National Chemical Laboratory, especially in respect of access to sources of published information in their possession.

The Editors wish also to put on record their continuing indebtedness to Messrs. Longmans Green & Co. Ltd. for the valuable advice and assistance they have most freely rendered. They would like to thank K.W. Allen for revising the late P.C.L. Thorne's manuscript on 'The Occurrence of Lithium'.

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Edition, Sodium (NaK) Supplement, July 1955*, published by the U.S. Atomic Energy Commission. Page 801, fig. 1; page 802, fig. 2 from Mott and Gurney, *Electronic Processes in Ionic Crystals*, published by the Clarendon Press. Page 448, fig. 2; page 476, fig. 5; page 476, fig. 6; page 477, fig. 7 from *N.R.L. Memorandum Report No. 33*, published by U.S. Naval Research Laboratory. Page 81, fig. 40; page 912, fig. 59 from J.C. Ricci, *Phase Rule and Heterogeneous Equilibria*, published by D. Van Nostrand Co. Inc. Page 852, Table XXX from H. Seidell, *The Solubilities of Inorganic and Metal Organic Compounds, Vol. I, 3rd. Edition*, published by the American Chemical Society. 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ABBREVIATIONS

absolute	abs.
alternating current	a.c.
ampere	amp.
Angstrom unit	A.
atmosphere-s (after a numeral)	atm.
atomic weight	at. wt.
boiling point	b.p.
British thermal unit	B.Th.U.
Calorie (large)	kg.-cal.
calorie (small)	g.-cal.
centimetre	cm.
cubic centimetre	c.c.
density (with a numeral)	ρ, *d.*
direct current	d.c.
electromotive force	e.m.f.
foot, feet	ft.
freezing point	f.p.
gram-s (with a numeral)	g.
hour-s (with a numeral)	hr.
inch-es	in.
kilogram	kg.
kilowatt	kW.
litre-s (with a numeral)	l.
melting point	m.p.
milliampere-s	ma.
millilitre-s	ml.
millivolt-s	mV.
minute-s	min.
molecular weight	mol. wt.
parts per million	p.p.m.
potential difference	p.d.
second-s (time only)	sec.
specific gravity	sp. gr.
square centimetre-s	sq. cm.
vapour density	v.d.
vapour pressure	v.p.
volt-s	V.
watt-s	W.
wave-length	λ

LIST OF ADDITIONAL LITERATURE ABBREVIATIONS

For uniformity, the literature abbreviations used in the references are the same as in *An Advanced Treatise on Physical Chemistry* by J.R. Partington, and in Supplement II, Part I of this work. In the list which follows, abbreviations are given only for those journals which do not occur in the above sources.

Abhl. Braunschweig. Wiss. Ges. Abhandlungen der braunschweigischen wissenschaftlichen Gesellschaft.

Abhl. Preuss. Akad. Wiss. Math. Klasse. Abhandlungen der preussichen Akademie der Wissenschaften, Mathematisch-naturwissenschaftliche Klasse.

Abstr. Comm. 1st Intern. Congr. Biochem. International Congress of Biochemistry, 1st Congress, Cambridge, England, 1949. Abstracts of Communications.

Abstr. Japan. Chem. Lit. Abstracts of Japanese Chemical Literature.

Acad. Rep. Populare Romîne, (Iaşi), Studii cercetări stiint. Academia republicii populare Romîne, Filiala Iasi, Studii si cercetari stiintifice. Bucharest.

Acad. Română Mem. sect. stiint. Academia Romana Memoriile sectiunii stiintifice. Bucharest.

Acad. Tchèque Sci., Bull. Intern., Classe Sci., Math., Nat. Med. Academia tchèque des sciences, Bulletin international, Resumés des travaux presentés, Classe des sciences, mathematiques, naturelles, et de la médecine.

Acta Agr. Scand. Acta Agriculturae Scandinavica. Stockholm.

Acta Agron. Acta Agronomica. Palmira, Columbia.

Acta Chim. Acad. Sci. Hung. Acta Chimica Academiae Scientiarum Hungaricae. Budapest.

Acta Endocrinol. Acta Endocrinologica. Copenhagen.

Acta Gastro-Enterol. Belg. Acta Gastro-Enterologica Belgica.

Acta Metallurgica. New York.

Acta Orthopaed. Scand. Acta Orthopaedica Scandinavica. Copenhagen.

Acta Path. Microbiol. Scand. Suppl. Acta Pathologica et Microbiologica Scandinavica. Copenhagen.

Acta Phys. Austriaca. Acta Physica Austriaca. Vienna.

Acta Physiol. Scand. Acta Physiologica Scandinavica. Copenhagen.

Acta Radiol. Acta Radiologica.

Acustica. Zurich.

Afinidad. Barcelona.

Agr. Gaz., N.S. Wales. Agricultural Gazette of New South Wales. Sydney.

Agricultura. Louvain, Belgium.

Agricultura Coloniale.

Agr. Res. Inst. Pusa, Sci. Repts. Agricultural Research Institute of Pusa, Scientific Reports.

Agrokemia.

A.I. Ch. E. Journal. American Institute of Chemical Engineers Journal.

A.I.M.E. Trans. American Institute of Metallurgical Engineers, Transactions.

Akad. Nauk. S.S.S.R. Pasiyyati S.I. Vavilova. Akademiya Nauk S.S.S.R. (Ed. S.I. Vavilova).

Allgem. Forstzeitschr. Allgemeine Forstzeitschrift. Munich.

Aluminium (Budapest).
Amer. Ceram. Soc. Bull. American Ceramic Society Bulletin. Columbus.
Amer. Foundryman. American Foundryman.
Amer. Heart J. American Heart Journal. St. Louis.
Amer. Inst. Chem. Eng. American Institute of Chemical Engineers.
Amer. J. Cancer. American Journal of Cancer.
Amer. J. Med. American Journal of Medicine. New York.
Amer. J. Obstet. Gynecol. American Journal of Obstetrics and Gynecology. St. Louis.
Amer. J. Physiol. American Journal of Physiology. Washington.
Amer. Perfumer. (See *Amer. Perfumer Essent. Oil Rev.*)
Amer. Perfumer Essent. Oil. Rev. American Perfumer and Essential Oil Review.
Amer. Ry. Eng. Assoc. Bull. American Railway Engineering Association Bulletins. Chicago.
Amer. Soc. Metals. American Society for Metals.
An. I. Congr. Pan-Amer. Ing. Minas y Geol. Santiago Chile. Anales del congreso panamericano de ingenieria de minas y geologia, 1st. Congress. Santiago.
An. Edafol. y Fisiol. Vegetal (Madrid). Anales de edafologia y fisiologia vegetal. Madrid.
An. Fac. Farm. y Bioquím., Univ. Nacl. Mayor San Marcos. Anales de la facultad de farmacia y bioquimica, Universidad nacional mayor de San Marcos. Lima.
An. Inst. Med. Exptl. Valencia. Anales del instituto de medicina experimental de Valencia.
An. Ofic. Quim. Prov. Buenos Aires. Anales de la oficina quimica de la provincia.
An. Real. Soc. Espan. Fis. Quim. Anales de la real sociedad espanola de fisico y quimica. Madrid.
Anat. Record. Anatomical Record, Philadelphia.
Ann. Acad. Brasil. Sci. Annaes da academia brasileira de sciencias.
Ann. Acad. Sci. Fenn. Annales Academiae Scientiarum Fennicae. Helsingfors.
Ann. Acad. Sci. Tech. Varsovie. Annales de l'academie des sciences techniques a Varsovie. Warsaw.
Ann. Agr. Coll. Sweden. Annals of the Agricultural College Sweden.
Ann. Agron. Anales Agronomiques. Paris.
Ann. Biol. Clin. Paris. Annales de biologie clinique. Paris.
Ann. Chim. Rome. Annali di chimica. Rome.
Ann. Chim. Phys. Annales de chimie et de physique. Paris.
Ann. Combustibles Liquides. Annales de l'office national des combustibles liquides. Paris.
Ann. École Nat. Agr. Montpellier. Annales de l'école nationale d'agriculture de Montpellier. Montpellier.
Ann. Endocrinol. (Paris). Annales d'endocrinologie. Paris.
Ann. Fac. Sci. Marseille. Annales de la faculte des sciences de Marseille.
Ann. Fac. Sci. Univ. Toulouse, Sci. Math. et Sci. Phys. Annales de la faculté des sciences de l'université de Toulouse pour les sciences mathematiques et les sciences physiques. Paris.
Ann. Gembloux. Annales de Gembloux. Belgium.
Ann. Geophys. Annales de geophysique. Paris.
Ann. Inst. Hydrol. et Climatol. Annales de l'institut d'hydrologie et de climatologie. Paris.
Ann. Inst. Mines Leningrad. Annales de l'institut Mines. Leningrad.
Ann. Inst. Pasteur. Annales de l'institut Pasteur. Paris.
Ann. Ist. Super. Agrar. Portici. Annali del r istituto superiore agrarian del Portici.

Ann. Postes, Teleg. Teleph. Annales des Postes, Télégraphie et Téléphonie.

Ann. Rep. Alkali etc., Works. Annual Report on Alkali etc., Works. London.

Ann. Rep. E. Malling Res. Sta. Annual Report, East Malling Research Station, Kent. Maidstone.

Ann. Rep. Mich. Acad. Sci. Annual Report of Michigan Academy of Science.

Ann. Rep. N.Y. State Assoc. Milk Sanitarians. Annual Report of the New York State Association of Milk Sanitarians.

Ann. Rep. Progr. Chem. Annual Reports on the Progress of Chemistry. London.

Ann. Rev. Nucl. Sci. Annual Review of Nuclear Science. California.

Ann. Sci. Annals of Science. London.

Ann. Sci. Agron. Annales de la science agronomique françaises et étranger.

Ann. Soc. Geol. Belg. Annales de la société géologique de Belgique.Bulletin. Liége.

Ann. Sper. Agrar. (Rome). Annali della sperimentazine agraria. Rome.

Ann. Staz. Sper. Agrar. Annali della r stazione sperimentale agraria di Modena. Modena. Italy.

Ann. Surg. Annals of Surgery. Philadelphia or Buenos Aires.

Ann. Univ. Mariae-Curie-Sklodowska Lublin-Polonia. Annales Universitatis Mariae-Curie-Sklodowska. Lublin. Poland.

Ann. Univ. Sofia (phys. math.). Annuaire de l'université de Sofia. Faculté Physico-Mathématique. Sofia.

Antibiotics and Chemotherapy. Washington.

Anz.-Akad. Wiss. Wien. Anzeiger der Akademie der Wissenschaften in Wien, Mathematisch-naturwissenschaftliche Klasse.

Apparatebau. Hanover.

Appl. Microbiol. Applied Microbiology. Baltimore.

Appl. Sci. Res. Applied Scientific Research. The Hague.

Aptechnoe Delo. Moscow.

Arch. Biochem. Biophys. Archives of Biochemistry and Biophysics. N. York.

Arch. farmacol. sper. Archivio di farmacologia sperimentale e scienze affini.

Arch. Gartenbau. Archiv fur Gartenbau. Berlin.

Arch. ges. Warmetech. Archiv für die gesamte Warmetechnik.

Arch. Ind. Health. Archives of Industrial Health.

Arch. Ind. Hyg. Occupational Med. Archives of Industrial Hygiene and Occupational Medicine.

Arch. Inst. farmacol. exptl. Archivos del instituto de farmacologie experimental. Madrid.

Arch. Internal Med. Archives of Internal Medicine. Chicago.

Arch. Intern. Physiol. Archives internationales de physiologie. Paris.

Arch. Ital. Malattie Apparato Digerente. Archivio italiano delle malattie dell'apparato digerente. Bologna.

Arch. Mikrobiol. Archiv fur Mikrobiologie. Berlin.

Arch. Mineralogiczne. Archiwum Mineralogiczne Towarzystwa Naukowego Warszawskiego.

Arch. Neerl. Phys. Archives néerlandais de physiologie de l'homme et des animaux.

Arch. Neurol. Pschyiatry. Archives of Neurology and Psychiatry. Chicago.

Arch. Ophthalmol. Archives of Ophthalmology. Chicago.

Arch. Pathol. Archives of Pathology. Chicago.

Arch. Suikerind. Archief voor Suikerindustrie in Nederlandsch-Indie.

Arch. Venezolanos Nutric. Archivos venesolanos de nutricion. Caracas.

Ariz. Bur. Mines, Mineral Technol. Bull. Arizona Bureau of Mines, Mineral Technology Bulletin.

Arkh. Biol. Nauk. Arkhiv Biologicheskikh Nauk. U.S.S.R.

Arkiv. Botan. Arkiv für Botani.

Arkiv Zool. Arkiv für Zoologi, utgivet av K. Svenska Vetenskapsakademien. Stockholm.

Arquiv. Biol. e Tecnol., Inst. Biol. e Pesquisas Tecnol. Arquivos de biologia e tecnologia, instituto de biologia e pesquisas tecnologicas. Parana.

Arquiv. Inst. Biol. São Paulo. Arquivos do instituto biologica. São Paulo.

Assoc. Tech. Ind. Papetière Bull. Association technique de l'industrie papetière Bulletin. Paris.

Asphalt Teerind. Ztg. Asphalt und Teerindustrie Zeitung und Zeitschrift für Strassenbau, Strassenunterhaltung sowie Tief und Bruckenbau.

A.S.T.M. Bull. American Society for Testing Materials Bulletin. Philadelphia.

Astron. J. Soviet Union. Astronomical Journal of the Soviet Union. Moscow.

Astron. Zhur. Astronomicheskii Zhurnal. Moscow.

Astrophys. Norvegica. Astrophysica Norvegica.

Atm. Energ. S.S.S.R. Atomic Energy U.S.S.R.

Atomics Eng. and Technol. Atomics, Engineering and Technology. London.

Atti Congr. Naz. Chim. Ind. Atti del congresso nazionale di chimica industriale. Milan.

Atti II Congr. Naz. Chim. Pura Applic. Atti del congresso naxionale di chimica pura ed applicata. Milan.

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Atti Soc. Nat. Mat. Modena. Atti della società dei naturalisti e matematici di Modena. Modena.

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Australasian Engr. The Australasian Engineer. Sydney.

Australia Bur. Min. Res., Geol. and Geophys. Summary Rep. Australia, Bureau of Mineral Resources, Geology and Geophysica. Summary Reports.

Australian Chem. Inst. J. and Proc. Australian Chemical Institute Journal and Proceedings.

Australian J. Appl. Sci. Australian Journal of Applied Science. Melbourne.

Australian J. Dairy Technol. Australian Journal of Dairy Technology. Melbourne.

Australian J. Sci. Australian Journal of Scientific Research. Melbourne.

Australian Pulp and Paper Ind. Tech. Assoc. Proc. Australian Pulp and Pape- Industry, Technical Association Proceedings.

Avtomobil. i Traktor. Prom. Avtomobil'naya i Traktornaya Promyshlennost. Moscow.

Avtogennoe Delo.

Baking Technology.

Beama J. The Beama Journal. London

Bell Telephone Quart. Bell Telephone Quarterly. New York.

Ber. D. botan. Ges. Berichte der deutschen botanischen Gesellschaft. Stuttgart.

Ber. ges. Physiol. exptl. Pharmakol. Berichte uber die gesamte Physiologie und experimentelle Pharmakologie. Berlin.

Bergbau. Bergbau Archiv. Essen.

Berg- und Hüttenmännisches Jahrb. Berg- und hüttenmännisches Jahrbuch der montanistischen Hochschule in Leoben. Vienna.

Better Crops with Plant Food. Washington.

Biochem. J. (Ukraine). Biochemical Journal (Ukraine).

Biol. Abstr. Biological Abstracts. Philadelphia.

Biol. Bull. Biological Bulletin. Massachusetts.

Biol. Rev. Biological Reviews of the Cambridge Philosophical Society. London.

Blast Furnace Steel Plant. Blast Furnace and Steel Plant. Pittsburg.

Bol. Acad. Nacl. Cienc. Córdoba. Boletin de la academia nacional de ciencias (Córdoba). Córdoba.

Bol. Inst. Geol. Espãna. Boletin del instituto geologico y minero de Espãna. Madrid.

Bol. Inst. Nacl. Invest. Agron. (Madrid). Bolétin del instituto nacional de investigaciones agronimicas. Madrid.

Bol. Min. Soc. Nacl. (Chile). Boletin minero (sociedad nacional de mineria, Santiago, Chile). Santiago.

Bol. Soc. Chilena Quim. Boletin de la sociedad chilena de quimica. Concepcion.

Bol. Soc. Nacl. Min. Boletin de la sociedad nacional de mineria del Peru. Lima.

Boll. Ist. Super Agrar. Pisa. Bollettino dell'istituto superiore agrario di Pisa.

Boll. Lab. Chim. Prov., Bologna. Bollettino dei laboratori chimici provinciali (Bologna).

Boll. Soc. Eustachiana. Bollettino della società eustachiana degli istituto scientifici dell'università di Camerino. Camerino.

Boll. Soc. Ital. Biol. Sper. Bollettino della società italianà di biologia sperimentale. Naples.

Bombay Technol. Bombay Technologist. Bombay.

Bot. Abstr. Botanical Abstracts.

Bot. Gaz. Botanical Gazette. Chicago.

Bot. Zhur. Botanicheskii Zhurnal. Moscow.

Bragantia. Brazil.

Braunkohlenarch. Das Braunkohlenarchiv, Vorkommen-Gewinnung-Verarbeitung-Verwendung der Brenstoffe.

Brit. Assoc. Adv. Sci. Rep. British Association for the Advancement of Science Report of the Annual Meeting.

Brit. Heart J. British Heart Journal. London.

Brit. J. Nutrition. British Journal of Nutrition. New York and London.

Brit. J. Phot. British Journal of Photography. London.

Brit. Med. Bull. British Medical Bulletin. London.

Bulgar. Akad. Nauk. Otdel. Geol.-Geograf. i Khim. Nauki, Izvest. Khim. Inst. Bulgarska Akadamiya na Naukite, Otdelenie za Geologo-Geografski i Khimicheski Nauki, Izvestiya na Khimicheskiya Institut.

Bull. Acad. Sci. Union Rep. Sov. Soc. Classe Sci. Phys.-Math. Bulletin de l'Académie des Sciences de l'Union des Républiques Sovietiques Socialistes. Classe des Sciences.

Bull. Amer. Assoc. Petroleum Geol. Bulletin of the American Association of Petroleum Geologists. Tulsa.

Bull. Amer. Meteorol. Soc. Bulletin of the American Meteorological Society. Boston.

Bull. Amer. Phys. Soc. Bulletin of the American Physical Society. New York.

Bull. Assoc. Chim. Sucr. Dist. Bulletin de l'Assocation des Chimistes de Sucrerie et de distillerie et des industries agricoles de France et des colonies.

Bull. Assoc. Franc. Tech. Pétrole. Bulletin de l'association françaises des techniciens du pétrole. Paris.

Bull. Central Electrochem. Res. Inst., Karaikudi. Bulletin of the Central Electrochemical Research Institute. Karaikudi. India.

Bull. Centre Belge Étude et Document. Eaux, Liége. Bulletin du centre belge d'étude et de documentation des eaux. Liége.

Bull. Chem. Res. Inst. Non-aq. Solns., Tohōku Univ. Bulletin of the Chemical Research Institute of Non-aqueous solutions, Tohōku University. Japan.

Bull. Chungking Inst. Ind. Res. Bulletin of Chungking Institute of Industrial Research, Ministry of Industry and Commerce. Chungking.

Bull. Classe Sci. Acad. Roy. Belg. Bulletin de la classe des sciences, Academie royale de Belgique. Brussels.

Bull. Electrotech. Lab. (Tokyo). Bulletin of the Electrotechnical Laboratory. Tokyo.

Bull. Eng. Res. Inst., Kyoto Univ. Bulletin of the Engineering Research Institute, Kyoto University.

Bull. Far Eastern Branch Acad. Sci. U.S.S.R. Bulletin of the Far Eastern Branch of the Academy of Sciences of the U.S.S.R.

Bull. Geol. Survey China. Bulletin of the geological survey of China. Nanking.

Bull. Govt. Res. Inst. Ceram.(Kyoto). Bulletin of Goverment Research Institute for Ceramics.

Bull. Histol. Appl. Path. Tech. Microscop. Bulletin d'histologie appliquée à la physiologie et à la pathologie et de technique microscopique.

Bull. India Sect. Electrochem. Soc. Bulletin of the Indian Section, the Electrochemical Society. Bangalore.

Bull. Inst. Agron. et Stas. Recherches Gembloux. Bulletin de l'institut agronomique et des stations de recherches de Gembloux. Gembloux.

Bull. Inst. Chem. Res. Kyoto Univ. Bulletin of the Institute for Chemical Research, Kyoto University.

Bull. Inst. Paper Chem. Bulletin of the Institute of Paper Chemistry.

Bull. Intern. Acad. Polonaise, Classe Sci. Math. et Nat. Bulletin International de l'académie polonaise des sciences et des lettres. Classe des sciences mathématiques et naturelles.

Bull. Japan. Soc. Sci. Fisheries. Bulletin of the Japanese Society of Scientific Fisheries. Tokyo.

Bull. Kobayashi Inst. Phys. Res. Bulletin of the Kobayashi Institute of Physical Research.

Bull. Res. Council Israel. Bulletin of the Research Council of Israel.

Bull. Res. Inst. Food Sci. Kyoto Univ. Bulletin of the Research Institute for Food Science, Kyoto University.

Bull. Res. Inst. Keikoku Jinzo Kenshi Kaisha Ltd. Bulletin of the Research Institute Keikoku Jinzo Kenshi Kaisha Ltd.

Bull. Soc. Chim. Romania, Bulletin de la Societe chimique de Romănia.

Bull. Soc. Chim. Roy. Yougoslav. Bulletin de la Societe Chimique du royaume de Yougoslavie.

Bull. Soc. Franç. Cer. Bulletin de la Société Française de céramique. Paris.

Bull. Soc. Franç. Min. Crist. Bulletin de la société Françaises de minéralogie et de cristallographie. Paris

Bull. Soc. Pharm. Bordeaux. Bulletin de la société de pharmacie Bordeaux.

Bull. Soc. Roum. Neurol., Psychiatrie, Physiologie Endocrinol. Bulletin de la société roumaine de neurologie, psychiatrie, physiologie et endocrinologie.

Bull. Soc. Sci. Bretagne. Bulletin de la société scientifique de Bretagne.

Bull. Soc. Sci. Hyg. Aliment. Bulletin de la société scientifique d'hygiene alimentaire et d'alimentation rationnelle de l'homme. Paris

Bull. State Inst. Marine Trop. Med. Gdansk. Bulletin of the State Institute of Marine and Tropical Medicine in Gdansk. Poland.

Bull. St. Francis Sanatorium. Bulletin of the St. Francis Hospital and Sanatorium, Roslyn, N.Y. New York.

Bull. Tech..A.I.Br. Bulletin technique A.I. Br. (association des ingenieurs sortis de l'universite libre de Bruxelles).

Bull. Tech. Univ. Istanbul. Bulletin of the Technical University of Istanbul.

Bumazh. Prom. Bumazhnaya Promyshlennost. Moscow.

Bur. Stand. Sci. Pap. Bureau of Standards Scientific Papers.

Buisseiron Kenkyû. Osaka Japan.

Cahiers Phys. Cahiers de physique. Paris.

Calif. Dept. Nat. Resources, Spec. Rept. Californian Department of Natural Resources, Special Report. San Francisco.

Canad. Chem. Prog. Canadian Chemical Progress.

Canad. Dept. Mines Tech. Surveys, Mines Branch, Topical Rept. Canadian Department of Mines and Technical Surveys, Mines Branch, Topical Report. Ontario.

Canad. J. Biochim. and Physiol. Canadian journal of Biochemistry and Physiology, Ottawa.

Canad. J. Med. Sci. Canadian Journal of Medical Science.

Canad. J. Phys. Canadian Journal of Physics. Ottawa.

Canad. Metals Met. Ind. Canadian Metals and MetallurgicalIndustries. Toronto.

Canad. Mining Met. Bull. Canadian Mining and Metallurgical Bulletin. Montreal.

Carnegie Inst. Technol. Tech. Rep. Carnegie Institute of Technology, Technical Report.

Casopis Lékářů Českých. Prague II, Czechoslovakia.

Cellulose Ind. (Tokyo). Cellulose Industry. Tokyo.

Centr. Bakt. Parisitenk. (See *Zent. Bakt. Parasitenk.*)

Centr. Natl. Recherche Sci. Groupe Franc. Argiles, Compt. Rend. Reunions Etudes. Centre national de la recherche scientifique, Group française des argiles, Compte rendu des reunions d'etudes. Paris.

Ceram. Abstr. Ceramic Abstracts.

Chem. Age. (India). Chemical Age of India. Bombay.

Chem. Age (N.Y.). Chemical Age, New York.

Chem. Bull. Chicago. Chemical Bulletin Chicago.

Chem. Eng. Prog. Symposium Ser. Chemical Engineering Progress Symposium Series. New York.

Chem. Eng. Prog. Symposium Ser. Ultrasonics. Chemical Engineering Progress Symposium Series. Ultrasonics. New York.

Chem. Eng. Sci. Chemical Engineering Science. New York.

Chem. High Polymers (Japan). Chemistry of High Polymers. Tokyo.

Chem. Ind. Chemische Industrie (Dusseldorf).

Chem. and Process Eng. Chemical and Process Engineering. London.

Chem. Průmsyl. Chemický Prumsyl.

Chemia (Buenos Aires). Buenos Aires.

Chimia (Switz.) Chimia (Switzerland) Zurich.

Chim. Chronika, Greece. Chimika Chronika. Athens.

Chim. Ind. Agr. Biol. Chimica nell'industria, nell'agricoltura, nella biologia e nelle realizzazioni corporative, La.

Ciel et Terre. Ciel et Terre. Uccle-Brussels.

Ciencia, Mex. Ciencia Mexico.

Circulation. New York.

Clay Minerals Bull. Clay Minerals Bulletin. Aberdeen.

Coke and Chem. U.S.S.R. Koks i Khimiya. Kharkov.

Cold Spring Harbor Symposia Quant. Biol. Cold Spring Harbor Symposia on Quantitative Biology. Long Island.

Coll. Chem. Colloid Chemistry. New York.

Coll. Intern. Centre Natl. Recherche Sci. (Paris). Colloques internationaux

Coll. Intern. Spectrographie Strasbourg. Colloque international de spectrographie de Strasbourg. Paris.

Colloq. Sensibilité Phot. Paris. Colloque Sensibilité Photographie. Paris.

Colon. Geol. Min. Res. Colonial Geology and Mineral Resources. London.

Comm. Fertilizer. Commercial Fertilizer. Atlanta.

Comm. Fertilizers Yearbook. Commercial Fertilizers Yearbook. Atlanta.

Complete Abstr. Japan. Chem. Lit. Complete Abstracts of Japanes Chemical Literatures. Sandai.

Compressed Air Mag. Compressed Air Magazine. Phillipsburg.

Compt. Rend. Acad. Agr. France. Comptes Rendus des séances de l'académie d'agriculture de France. France.

Compt. Rend Acad. Sci. U.R.S.S. Comptes Rendus (Doklady) de l'académie des sciences de l'U.R.S.S.

Compt. Rend. 27 Congr. Intern. Chim. Ind. Brussels. Comptes rendus des congrès internationaux de chimie industrielle 27 Congrès Brussels. 1954.

Compt. Rend. 78 Congr. Socs. Savantes Paris et Depts. Sect. Sci. Comptes rendus du congrès des sociétés Savantes de Paris et des départements, Section des sciences. 78 Congrès.

Compt. Rend. Soc. Geol. Finlande. Compte Rendu sommaire des séances de la société géologique de Finlande.

Compt. Rend. Trav. Lab. Carlsberg, Sér. Chim. Comptes rendus des travaux du laboratoire Carlsberg, série chimique. Copenhagen

Concrete (Cement Mill Section). Concrete. Chicago.

14 Congr. Chim. Ind. Paris. Congrès de chimie industrielle.

Congr. Groupe. Avance. Method. Anal. Spectrograph. Produits Met. Congrès du groupement pour l'avancement des méthodes d'analyse spectrographique des produits metallurgiques. Arcueil. France.

IX Congr. Intern. Quím. Pura Aplicada, Madrid. Congreso internacional de química pura y aplicada. 9th Congress. Madrid.

Congrès Internat. du Froid. Congrès Internationale du Froid. Paris.

Conn. Agr. Expt. Sta. (New Haven) Bull. Connecticut Agricultural Experimental Station, New Haven Bulletin. New Haven.

Contrib. Perkins Observatory, Ohio Wesleyan Univ. and Ohio State Univ. Contributions from the Perkins Observatory, Ohio Wesleyan University and Ohio State University. Delaware.

Corrosion Prevention and Control. London.

Corrosion Tech. Corrosion Technology, London.

Cotton Oil Press. Dallas.

Cuoio Pelli Mat. Concianti. Cuoio, pelli, materie concianti. Naples.

Cuir Tech. Le Cuir technique.

Cukoripar. Budapest.

Czech. J. Phys. Czechoslovak Journal of Physics.

Das Leder. Germany.

De Ingenieur. Utrecht. Netherlands.

Del. Agr. Expt. Sta. Tech. Bull. Agricultural Experimental Stations of Delaware. Technical Bulletin. Delaware.

Demir ve Celik. Karabuk. Turkey.

Dept. Agr. Union S. Africa Science Bull. Department of Agriculture, Union of South Africa, Science Bulletin. Pretoria.

Dept. Sci. Ind. Res. (Brit.) Water Pollution Res. Summary Current Lit. Department of Scientific and Industrial Research (Britain) Water Pollution Research, Summary of Current Literature. London.

Deut. Arch. klin. Med. Deutsches Archiv fur klinische Medizin. Munich.

Deut. Baumwollind. Deutsche Baumwollindustrie. Germany.

Deut. Farber-Ztg. Deutsche Farber-Zeitung vereinigt mit der Leipziger Farber und Zeugdrucker-Zeitung. Stuttgart.

Deut. Farben-Z. Deutsche Farben Zeitschrift. Stuttgart.

Deut. Landw. Presse. Deutsche landwirtschaftliche Presse vereinigt mit Illustrierte landwirtschaftliche Zeitung. Frankfurt.

Deut. Textilgewerbe. Deutsche Textilgewerbe. Düsseldorf.

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Die Medizinische. Berlin.

Diss. Abstr. Dissertation Abstracts. Ann Arbor.

Dominion Astrophys. Obs. Victoria Publ. Dominion Astrophysical Observatory, Victoria, Publications. Ottawa.

Dow Diamond. London.

Drug. Standards. Washington.

D.S.I.R. Water Pollution Res. Summ. Department of Scientific and Industrial Research. Water Pollution Research Summary of Current Literature.

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Eau. Eau, L., Revue mensuelle de l'eau potable et de l'assainissement. Apparently suspended with Vol. 32, No. 8(Aug. 1939). Appeared again in 1946. Paris.

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Electroplating and Metal Finishing. Middlesex, England.

Elektrowärme. Essen and Hanover.

Enamelist. The Enamelist. Cleveland, Ohio.

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Eng. Mining-J. Press. Engineering and Mining-Journal Press. New York.

Eng. News-Record. Engineering News-Record. Albany, New York.

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Ernähr. Pflanze. Die Ernährung der Pflanze. Berlin, Germany.

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Excerpta Med. Excerpta Medica. New York.

Exposés Annuels Biochim. Med. Exposés Annuels de biochimie médicale. Paris.

Exptl. Med. Surg. Experimental Medicine and Surgery. New York.

Expt. Sta. Record. Experiment Station Record. New York.

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Faculty Sci. Agr., Taihoku Imp. Univ. Faculty of Science and Agriculture, Taihoku Imperial University.

Farmácia. Bratislava, Czech.

Farm. Chilena. Farmacia Chilena. Santiago, Chile.

Farm. Moderna. Farmacia Moderna. Santiago, Chile.

Farmacognosia.

Faserforsch. u. Textiltech. Faserforschung und Textiltechnik. Berlin.

Fertilizer, Feeding Stuffs and Farm Supplies J. Fertilizer, Feeding Stuffs and Farm Supplies Journal. London.

Fette-Seifen-Anstrichmittel. Hamburg.

Fette u. Seifen Anstrichmittel. Fette und Anstrichmittel. [Name changed to *Fette-Seifen-Anstrichmittel,* Which see].

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Fischwirt. Fischwirtschaft. Berlin.

Fluid Handling. London.

Folia Endocrin. Pisa. Folia Endocrinologica. Pisa, Italy.

Folia Pharmacol. Japon. Folia Pharmacologica Japonica. Tokyo.

Fonderie. Paris.

Food Eng. Food Engineering. (Formerly *Food Inds.*). New York.

Food Packer. (Formerly *Food Packing and Canning Age*), Chicago

Food Research. Champaign, Ill.

Food Technol. Food Technology. Champaign, Ill.

Foote Prints. U.S.A.

Frieberg. Forsch. Frieberger Forschungshefte. Berlin

Gas. Los Angeles, California.

Gaz. Cukrownicza. Gazeta Cukrownicza. Warsaw.

Geochim. Cosmochim. Acta. Geochimica et Cosmochimica Acta. London and New York.

Geol. Geology.

Geol. Mag. The Geological Magazine. Hertford, Herts.

Geologi. Helsinki, Finland.

Geophys. Publikasjoner, Norske Videns.-Akad., Oslo. Geophysiske Publikasjoner, Norske Videnskaps-Akademi i Oslo. Oslo, Norway.

Gidrokhim. Materialy, Akad. Nauk S.S.S.R. Gidrokhimicheskie Materialy, Akademii Nauk S.S.S.R. Moscow.

Giessen Oberhess. Ges. Ber. Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen, Naturwissenschaftliche Abeilung. Giessen.

Glastek. Tidskr. Glasteknik Tidskrift. Vaxjo 3, Sweden.

Glas-Email-Keramo-Tech. Glas-Email-Keramo-Technik. Postfach, Germany.

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Glass Ind. Glass Industry. New York.

Glückauf. Essen, Germany.

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Gornuii Zhur. Gornuii Zhurnal. Moscow.

Gosudarst. Inst. Prikladnoĭ Khim., Sbornik Statei. Gosudarstvennyĭ Institut Prikladnoĭ Khimii, Sbornik Statei. Moscow.

Gosudarst. Vsesoyuz. Inst. Proektviovaniyu Predpriyatiĭ i Nauch.- Issledovatel. Rabote Tsement. Prom., "Giprotsement," Trudy. Gosudarstvennyĭ Vsesoyuznyi Institut po Proektirovaniyu Predpiryati i po Nauchno-Issledovatel'skoi Rabote i Tsementnoi Promyšhlennosti "Giprotsement," Trudy.

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Hadar. Absorbed by the *Palestine Tribune.*

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Helv. Physiol. Pharmacol. Acta. Helvetica Physiologica et Pharmacologica Acta. Basel.

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Hist. de l'Inst. See *Mem. de l'Inst.*

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Humus. Milan.

Hung. Acta Physiol. Hungarica Acta Physiologica. Hungary.

Hutnické Listy. Prague, Czech.

Hutnik. Warsaw.

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Ind. Agr. et Aliment. (Paris). Industries agricoles et alimentaires (Paris).

Ind. Chim. Industrie Chimique. Paris.

Ind. Eng. Chem. News Ed. Industrial and Engineering Chemistry. News Edition. See *Chem. Eng. News.*

Ind. Finishing (London). Industrial Finishing (London).

Ind. Saccar. Ital. Industria Saccarifera Italiana. Genoa.
Ind. Safety Survey. Industrial Safety Survey.
Ind. Textile. Industria Textile. Paris.
Ind. Usoară (Bucharest). Industria Usoară (Bucharest).
Ind. Vernice, Milan. L'Industria della Vernice. Milan.
Indian Farming. New Delhi.
Indian J. Med. Res. The Indian Journal of Medical Research. Cawnpore.
Indian J. Res. Indian Journal of Research.
Indian Soap J. Indian Soap Journal. Calcutta.
Industria Carta (Milan). Industria della Carta, Milan, Italy.
Industria Ital. Conserve. L'Industria Italiana delle Conserve. Parma, Italy.
Industria y Química. Buenos Aires.
Industrie Céram. Industrie Cerãmique. Paris.
Ing. Chim. Ingegneria Chimica. Milan.
Ingeniøren. Copenhagen, Denmark.
Inst. Chem. Eng. Institution of Chemical Engineers. London.
Inst. Intern. Phys. Solvay 4th. Conseil. Institut International de Physique Solvay, 4th Conseil. Brussels, Belgium.
Inst. Mech. Eng. (London), Applied Mechanics Proc. Proceedings of the Institute of Mechanical Engineers (London). Applied Mechanics.
Inst. Roy. Colonial Belge, Sect. Sci. Tech., Mém. Institut Royal Colonial Belge. Section of Science and Technology. Mémoir. Brussels.
Instruments. Pittsburgh, Pa.
Inter. Astronaut. Congr. 3rd. Congr. Stuttgart, Ger. International Astronautical Congress, 3rd. Congress. Stuttgart, Germany.
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Iva. Stockholm, Sweden.
Iwata Inst. Plant Biochem. Iwata Institute of Plant Biochemistry. Japan.
Izvest. Akad. Nauk Armyan. S.S.R., Ser. Fiz.-Mat. Estestven. i Tech. Nauk. Izvestiya Akademii Nauk Armyanskoi S.S.R., Fiziko-Matematicheskie, Estestvennye i Tekhnicheskie Nauki.
Izvest. Akad. Nauk Kazakh. S.S.R., No. 123, Ser. Khim. Izvestiya Akademii Nauk Kazakhskoĭ S.S.R., No. 123, Seriya Khimicheskaya.
Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk. Izvestiya Akademii Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk. Moscow, U.S.S.R.
Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk Tekh. Izvestiya Akademii Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk Tekhnicheskikh. Moscow.

Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk. Izvestiya Akademii Nauk S.S.S.R., Otdelenie Tekhnicheskikh Nauk. Moscow.

Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. Izvestiya Akademii Nauk S.S.S.R., Seriya Fizicheskaya. Moscow.

Izvest. Fiz.-Khim. Nauch.-Issledovatel. Inst. Irkutsk Univ. Izvestiya Fiziko-Khimicheskikh Nauchno-Issledovatel'skogo Instituta Irkutsk-Universitete. Moscow.

Izvest. Polytechn. Inst. Novocherkassk. Izvestiya Polytechnicheskogo Instituta Novocherkassk. Moscow.

Izvest. Sekt. Fiz.-Khim. Anal. Akad. Nauk S.S.S.R. Izvestiya Sektora Fiziko Khimicheskogo Analiza, Akademiya Nauk S.S.S.R. Moscow.

Izvest. Sekt. Fiz.-Khim. Anal. Inst. Obshcheĭ i Neorg. Khim. Akad. Nauk S.S.S.R. Izvestiya Sektora Fiziko-Khimicheskaya Analiza, Institut Obshcheĭ i Neorganicheskoĭ Khimii imeni N. S. Kurnakova, Akademiya Nauk S.S.S.R. Moscow.

Izvest. Sekt. Platiny i Drug, Blagarod. Metal., Akad. Nauk S.S.S.R., Inst. Obshcheĭ i Neorg. Khim. Izvestiya Sektora Platiny i Drugykh Blagarodnykh Metallov, Institut Obshcheĭ i Neorganicheskoĭ Khimii imeni N. S. Kurnakova, Akademiya Nauk S.S.S.R. Moscow.

Izvest. Timiryazev. Sel'skokhoz. Akad. Izvestiya Timiryazevskoĭ Sel'Skokhozyaistvennoĭ Akademii. Moscow.

Izvest. Tomsk. Politekh. Inst. Izvestiya Tomskogo Politekhnicheskogo Instituta. Tomsk, U.S.S.R.

J. Agr. Food Chem. Journal of Agricultural and Food Chemistry. Washington.

J. Amer. Concrete Inst. Journal of the American Concrete Institute. Detroit.

J. Amer. Dental Assoc. Journal of the American Dental Association. Chicago.

J. Amer. Dietet. Assoc. Journal of the American Dietetic Association. Chicago, Illinois.

J. Anal. Chem. U.S.S.R. The Journal of Analytical Chemistry of the U.S.S.R.

J. and Proc. Indian Chem. Soc. Journal and Proceedings of the Indian Chemical Society. Calcutta.

J. Antibiotics (Japan). Journal of Antibiotics (Japan). Tokyo, Japan.

J. Appl. Physiol. Journal of Applied Physiology. Washington.

J. Australian Inst. Med. Journal of the Australian Institute of Metals. Victoria.

J. Birmingham Met. Soc. Journal of the Birmingham Metallurgical Society. Birmingham.

J. Bombay Nat. Hist. Soc. Journal of the Bombay Natural History Society.

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J. Chem. Eng. (China). The Journal of Chemical Engineering. Chekiang.

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J. Clin. Invest. The Journal of Clinical Investigation. New York.

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J. Dept. Agr. Victoria. Journal of the Department of Agriculture, Victoria.

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J. Electrochem. Soc. Japan. Journal of the Electrochemical Society, Japan. Tokyo.

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J. Gerontol. Journal of Gerontology. St. Louis.
J. Hyderabad Geol. Survey. Journal of the Hyderabad Geological Survey. Deccan, India.
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J. Investigative Dermatol. Journal of Investigative Dermatology. Baltimore, Md.
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Jahrb. Hallesches Verband. Erforsch. Mitteldeut. Bodenschätze. Hallesches Jahrbuch für Mitteldeutsche Erdgeschichte. Halle, Germany.

Jahrb. Preuss. Geol. Landesanstalt. Jahrbuch der Preussischen Geologischen Landesanstalt. Berlin.

Jahresber. Limnol. Flussta Freudenthal. Jahresbericht Limnologie Flussta Freudenthal.

Jahresheft Geol. Abt., Wurttemberg Statist. Landesamtes. Jahresheft Geol. Abteilung, Wurttemberg Statistisches Landesamtes.

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K. Akad. Wetenschappen, Amsterdam Proc. Konelige Akademiens Wetenschappen, Amsterdam. Proceedings.

K. Norsk. Vidensk. Selsk. Forhl. Kongelige Norske Videnskabernes Selskabs. Forhandlinger, Tondheim.

Kagaku. Kyoto and Tokyo. (Japan).

Kali u. Steinsalz. Kali und Steinsalz. Essen, Germany.

Keemia Teated. Bratislava.

Kem. i Ind. (Zagreb). Kemija i Industriya (Zagreb). Yugoslavia.

Kem. Zbornik. Kemijski Zbornik. Yugoslavia.

Keram. Rundschau. Keramische Rundschau. Koslar, Germany.

Kgl. Dansk. Videns. Selskab. Biol. Medd. Det Kongelige Danske Videnskabernes Selskab, Biologiske Meddelelser. Copenhagen.

Kgl. Dansk. Videns. Selskab. Mat. Fys. Medd. Det Kongelige Danske Videnskabernes Selskab, Matematisk-Fysike Meddelelser. Copenhagen.

Kgl Landtbrucks-Akad. Handl. Tid. Kungliga Landtbrucks-Akademiens Handlingar och Tidskrift. Copenhagen.

Kgl. Landtbrucks-Högskol. Ann. Kungliga Landtbrucks-Högskolans Annalen. Uppsala, Sweden.

Khim. i Ind. Khimiya i Industriya. Sofia, Bulgaria.

Khim. Redkikh Elementov, Akad. Nauk S.S.S.R., Inst. Obshcheĭ i Neorg. Khim. Khimiya Redkikh Elementov, Akademiya Nauk S.S.S.R., Institut Obshcheĭ i Neorganicheskoĭ Khimiĭ. Moscow.

Khim. Referat. Zhur. Khimicheskiĭ Referativnyĭ Zhurnal.

Khlopchatobumazh. Prom. Khlopchatobumazhnaya Promyshlennost. Moscow.

Kholodil'naya Tekh. Kholodil'naya Tekhnika. Moscow.

Kim. Inst. Zinātnisk. Raksti, Latvijas P.S.R. Zinātnu Akad. Kimijas Instituta Zinǎtniskie Raksti, Latvijas P.S.R. Zinǎtnu Akademija.

Koll. Zhur. Kolloidnyĭ Zhurnal.-Moscow.

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Koninkl. Nederland. Akad. Wetenschap., Proc. Koninklijke Nederlandse Akademie van Wetenschappen, Proceedings.

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Laboratorio. Granada, Spain.
Landbouw. Djakarta. Indonesia.
Landbouwkund. Tidschr. Landbouwkundig Tidschrift. The Hague.
Landw. Jahrb. für Bayern. Landwirtschaftliches Jahrbuch für Bayern.
Landw. Jahrb. Schweiz. Landwirtschaftliches Jahrbuch der Schweiz. Bern.
La Ceramica. Rome and Milan.
Latvijas PSR Zinatnu Akad. Vestis. Latvijas PSR Zinatnu Akademijas Vestis. Riga, U.S.S.R.
Leather and Shoes. Chicago.
Ledertech. Rundschau. Ledertechnische Rundschau. Berlin.
Legkaya Prom. Legkaya Promyshlennost. Moscow.
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Liebigs Ann. Liebigs Annalen für Chemie. (See *Annalen*).
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Louisiana Planter. U.S.A.
Maden Tetkik Arama. Maden Tetkik ve Arama Enstitusu Mecmuasi. Ankara.
Magyar Kém. Folyőirat. Magyar Kémiai Folyőirat. Budapest.
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Manitoba Dept. Mines and Nat. Resources, Mines Branch Publ. Manitoba Department of Mines and Natural Resources, Mines Branch Publications.
Maslobořno-Zhirovaya Prom. Maslobořno-Zhirovaya Promyshlennost. Moscow.
Maslobořno Zhirovoe Delo. See *Maslobořno-Zhirovaya Prom.*
Mass. Inst. Tech. Res. Lab. Electronics Tech. Rep. Massachusetts Institute of Technology, Research Laboratory of Electronics and Lincoln Laboratory Technical Report.
Mass. Inst. Technol. Rept. K. 729. Massachusetts Institute of Technology, Report K. 729. Massachusetts.
Materials and Methods. New York.
Materiaux Géol. Génèrale et Appliqué, Leningrad. Materiaux Géologiques et Applique, Leningrad.
Materie Plastiche. Milan
Mazda Kenkyu Jiho. Japan.
Mécanique. Paris.
Mech. Eng. Mechanical Engineering. Easton. Pa.
Med. Doświadczalna i Mikrobiol. Medycyna Doświadczalna i Mikrobiologia. Warsaw.
Med. Sper. Medicina Sperimentale. Turin.
Medd. Lunds Geol.-Mineral. Inst. Meddelanden fran Lunds Geologisk-Mineralogiska Institution, Lund. Sweden.
Medel. Landbouwhogeschool Opzoekingsstas. Staat Gent. Mededelingen van de Landbouwhogeschool en de Opzoekingsstations van de Staat te Gent. Gent. Belgium
Mém. Assoc. Ing. Ecolê Liége. Mémoires de l'association Ingénieure, Ecolê Liége.
Mem. Assoc. Tecnicos Azucar. Cuba. Memoria de la associacion de tecnicos azucareros de Cuba.

Mem. Fac. Eng. Kyoto Univ. Memoirs of the Faculty of Engineering Kyoto University. Kyoto. Japan.

Mem. Fac. Eng. Kyushu Univ. Memoirs of the Faculty of Engineering Kyushu University. Fukuoka. Japan.

Mem. Inst. Sci. Ind. Res. Osaka Univ. Memoirs of the Institute of Scientific and Industrial Research, Osaka University. Osaka. Japan.

Mem. Proc. Manchester Lit. and Phil. Soc. Memoirs and Proceedings of the Manchester Literary and Philosophical Society. Manchester.

Mem. Rev. Soc. Cien. Memorias y revista de la sociedad cientifica Antonio Alzate. Mexico.

Mém. Services Chim. État, Paris. Mémorial des services chimiques de l'état. Paris.

Mém. Soc. Sci. Liége. Mémoires de la société des sciences de Liége. Liége.

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Metal Finishing. Westwood. N. Jersey.

Metal. Abs. Metallurgical Abstracts. London.

Met. Ital. Metallurgia Italiana. Milan. Italy.

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Metal. Ind. Co. Chem. Abs. The Metal Industry Co. Chemical Abstracts.

Metall. Grunewald. Germany.

Metalloberfläche. Munich.

Metallurgie u. Giesssereitech. Metallurgie und Giesssereitechnik.

Métaux. (Corrosion-Inds.) Combination of Métaux & Corrosion and Métaux & Industries. Seine-et-Oise. France.

Metody i Protsessy Khim. Tekhnol. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk Sbornik. Metody i Protsessy Khimicheskoi Tekhnologii, Akademiya Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk, Sbornik. Moscow.

Metropol. Mus. (New York) Report. Metropolitan Mus Report. New York.

Mezögazdasági Kutatások. Budapest.

Mikrochem. Emich Festschr. Mikrochemie Emich Festschrift.

Mikrochemie ver. Mikrochim. Acta. Mikrochemie vereinigt mit Mikrochimica Acta. Vienna.

Mikrokosmos. Stuttgart.

Milchw. Forsch. Milchwirtschaftliche Forschungen.

Milchwissenschaft. Nuremburg.

Mine and Quarry Eng. Mine and Quarry Engineering. London.

Mineralog. Abstr. Mineralogical Abstracts. London.

Mineral. Mag. The Mineralogical Magazine and Journal of the Mineralogical Society. London.

Minerva Pediat. Minerva Pediatrica. Turin.

Mining Congress J. Mining Congress Journal. Washington.

Mining Eng. Mining Engineering. New York.

Mining J. (London). Mining Journal. London.

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Misc. Phys. and Chem. Techniques. Miscellaneous Physical and Chemical Techniques. London.

Misc. Publ. Miscellaneous Publications (of the International Tin Research and Development Council). Middlesex, England or Columbus, Ohio.

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Mitt. deut. Materialprufungsanstalt. Mitteilungen der deutschen Materialprufungsanstalten. Frankfurt-am-Main.

Mitt. Med. Akad. Kioto. Mitteilungen aus der Medizinischen Akademie zu Kioto. Kyoto, Japan.
Mitt. Ver. Grosskesselbesitzer. Mitteilungen der Vereinigung der Grosskesselbesitzer. Dusseldorf, Germany.
Modern Plastics. New York.
Modern Refrig. Modern Refrigeration. London.
Mokuzai Kenkyu. Kyoto, Japan.
Molochnava Prom. Molochnaya Promyshlennost. Moscow.
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Mosskulturforehingens Svenska Tids. Mosskulturforenhingens Svenska Tijdschriftoch Mosskveturföreningens Meddelanden.
Myasnaya Ind. S.S.S.R. Myasnaya Industriya S.S.S.R. Moscow.
Nachr. Akad. Wiss. Göttingen, Math.-Phys. Klasse IIa. Math.-Phys.-Chem. Abt. Nachrichten der Akademie der Wissenschaften in Göttingen, Mathematisch-Physikalische. Klasse IIa. Mathematisch-Physikalisch-Chemische Abteilung. Göttingen, Germany.
Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, Fachgruppe II. Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse, Fachgruppen II. Göttingen, Germany.
Nafta (Yugoslavia). Zagreb, Yugoslavia.
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Nauk. Zapiski Tzukrovoĭ Prom. Naukovi Zapiski z Tzukrovoĭ Promislovosti.
Nauk. Zapysky L'viv. Derzhavnogo Univ. im. Ivana Franka. Naukovi Zapiski, L'vivs'kiĭ Derzhavniĭ Universitet imeni Ivana Franka. Lvov, Ukr. S.S.R.
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Nord. Kemikermøde, Förh. Nordiske Kemikermøde, Förhandlingar.
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Nova Proizvodnja. Ljubljana, Yugoslavia.
Novosti Neftyanoĭ Tekh. Neftepromyslovoe Delo. Novosti Neftyanoĭ Tekhniki. Neftepromyslovoe Delo.
Novosti Tekh., Ser. Gornorudnaya Prom. Novosti Tekhniki, Series, Gornorudnaya Promyshlennost. Moscow.
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Obstet. Gynecol. Survey. Obstetrical and Gynecological Survey. Baltimore, Md.
Occupational Hazards. Cleveland, Ohio.
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Onderzoekingen Physiol. Lab., Ulrecht. Onderzoekingen van den Physiologische Laboratorium, Ulrecht.

Onderz. Physiol. Scheikunde. Onderzoekingen van Physiologische Scheikunde.
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Österr. Akad. Wiss. Österreichische Akademie der Wissenschaften. Vienna. Austria.
Österr. Akad. Wiss., Math.-Naturw. Klasse, Anz. Österreichische Akademie der Wissenschaften, Mathematisch-Naturwissenschaftliche Klasse, Anzeiger. Vienna, Austria.
Österr. Leder-Ztg. Österreichische Leder-Zeitung. Vienna, Austria.
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Paper Makers' Monthly J. Paper Makers' Monthly Journal.
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Papier-Fabr. Der Papier-Fabrikant.
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Pharm. Presse. Pharmazeutische Presse.
Pharm. Zentralhalle. Pharmazeutische Zentralhalle für Deutschland. Dresden. Germany.
Philips Tech. Rundschau. Philips Technische Rundschau. Eindhoven, Netherlands.
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Phot. Chronik. Photographische Chronik.
Phot. Ind. Photographische Industrie.
Phot. Ind. (Japan). Photographic Industries. Tokyo, Japan.
Photographe. Paris.
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Pishchevaya Prom. Pishchevaya Promyshlennost. Moscow.
Pittsburgh Plate Products.
Pitture e vernici. Milan, Italy.
Planter Sugar Mfr. Planter and Sugar Manufacturer. London.
Plating. New Jersey.
Pochvovednie. Moscow.
Pogg. Ann.
Policlinico, Sez. Prat. Policlinico, Sezione Pratica. Rome, Italy.
Polish Agr. Forest Ann. Polish Agricultural and Forest Annual.
Polska Akad. Umiejetnośći. Polska Akademia Umiejetnośći. Cracow, Poland.

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Poznań. Towarz. Przyjaciót Nauk, Prace Komisji Med. Doświadczalnej. Poznańskie Towarzystwo Przyjaciót Nauk, Prace Komisji Medycyny Doświadczalnej. Poznan, Poland.

Prace Głównego Inst. Chem. Przemyst. Prace Głównego Instytutu Chemii Przemystowej. Stalinogród, Poland.

Prace Inst. Ministerstwa Hutnictwa. Prace Instytutow Ministerstwa Hutnictwa. Stalinogród, Poland.

Prace Placówek Nauk-Badawcz. Ministerstwa Przemystu Chem. Prace Placówek Naukowo-Badawczych Ministerstwa Przemystu Chemicznego. Warsaw, Poland.

Prakt. Chem. Praktische Chemie. Vienna.

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Proc. Leningrad Dept. Inst. Fert. Proceedings of the Leningrad Institution. Department for Fertilisers.

Proc. 6th. Meeting Intern. Comm. Electrochem. Thermodynam. and Kinet. Proceedings of the 6th. Meeting of the International Committee of Electrochemical Thermodynamics and Kinetics.

Proc. N.B.S. Semicentennial Symposium Low-Temp., Phys. Nat. Bur. Stand. Proceedings of the National Bureau of Standards. Semicentennial Symposium at Low-Temperature.

Proc. Phys. Soc. Proceedings of the Physical Society. London.

Proc. 7th. Pacific Sci. Congr., New Zealand. Proceedings of the 7th. Pacific Science Congress, New Zealand.

Proc. Phys. Soc. Japan. Proceedings of the Physical Society of Japan. Tokyo.

Proc. Roy. Acad. Amsterdam. Proceedings of the Royal Academy of Amsterdam.

Proc. S. African Sugar Technol. Assoc. Proceedings of the South African Sugar Technologists' Association. Johannesburg.

Proc. Sci. Assoc., Maharajah's Collegem Vizianagram. Proceedings of the Scientific Association, Maharajah's College, Vizianagram.

Proc. S. Dakota Acad. Sci. Proceedings of the South Dakota Academy of Science. South Dakota.

Proc. Soc. Promotion Agr. Sci. Proceedings of the Annual Meeting of the Society for the Promotion of Agricultural Science.

Proc. Sugar Technol. Assoc., India. Proceedings of the Sugar Technologists' Association, India. Kanpur, India.

Proc. Tech. Sect., Brit. Paper and Board Makers' Assoc. Proceedings of the Technical Section, Paper and Board Makers' Association of Great Britain and Ireland.

Proc. Trans. Nova Scotian Inst. Sci. Proceedings and Transactions of the Nova Scotian Institute of Science. Halifax, Nova Scotia.

Proc. Utah Acad. Sci. Proceedings of the Utah Academy of Sciences, Arts, and Letters. Logan, Utah.

Proc. Yale Mineralog. Soc. Proceedings of the Yale Mineralogical Society.

Proc. Yorkshire Geol. Soc. Proceedings of the Yorkshire Geological Society. Leeds, England.

Proc. Zeeman Congr. Amsterdam. Proceedings of the Zeeman Congress, Amsterdam.

Producers' Monthly. Bradford, Pa.

Progr. Agr. Vit. Progrès agricole et viticole. Montpellier.

Progr. Nuclear Phys. Progress in Nuclear Physics. New York.

Protoplasma. Vienna, Austria.

Prov. Saskatchewan, Dept. Mineral Resources, Ind. Minerals Research Branch. Rep. Invest. Province of Saskatchewan, Department of Mineral Resources, Industry and Minerals Research branch. Report of Investigation. Saskatchewan, Canada.

Przeglad Gorniczo-Hutniczy. Poland.

Przeglad Górniczy. Warsaw, Poland.

Przeglad Papier. Przeglad Papierniczy. Lodz. Poland.

Przeglad Sbórzany. Lodz, Poland.

Pub. Astron. Soc. Pacific. Publications of the Astronomical Society of the Pacific. San Francisco, California.

Pub. Dominion Astrophys. Observatory, Victoria, B.C. Publications of the Dominion Astrophysical Observatory, Victoria, B.C. Ottawa, Canada.

Pub. Faculté Sci. Univ. Masaryk. Publications de la faculté des sciences de l'université Masaryk. Moraira, Czech.

Pub. Inst. Invest. Microquim., Unic. Nacl. Litoral. Publicaciones del instituto de investigaciones microquimicas, Universidad Nacional del Litoral. Rosario, Republic of Argentina.

Pub. Inst. Quim. "Alonso Barba". Publicaciones del instituto de quimica "Alonso Barba". Madrid.

Pub. Sci. Tech. Ministère air. Publications scientifiques et techniques du ministère de l'air. France.

Public Roads. Washington, D.C.

Pulp and Paper. San Francisco, California.

Quart. J. Indian Inst. Sci. Quarterly Journal of the Indian Institute of Science. Bangalore, India.

Raboty Khim. Rastvorov i Kompleks. Soedinenii, Akad. Nauk U.S.S.R. Raboty po Khimii Rastvorov i Kompleksnykh Soedinenii, Akademiya Nauk Ukrainskoi S.S.R. Kiev.

Radex Rundschau. Austria.

Rad. Acad. Sci. Zagreb. Radovi Academie (of Science) Zagreb.

Radiology. New York.

Rapport Proefstation Aardappelverwerk.

Rass. Chim. (Rome). Rassegna Chimica. Rome.

Rass. di Studi Psichiatrici. Rassegna di Studi Psichiatrici. Siena, Italy.

Rass. Min. Met. Chim. Rassegna mineraria, metallurgica e chimica. Italy.

Rayon Melliand Textile Monthly.

Rayon Record. Manchester.

Rayon Textile Monthly.

Records Geol. Survey, India. Records of the Geological Survey of India. Calcutta.

Redkie Metal. Redkie Metally. Moscow.

Referat. Zhur. Khim. Referaturnyi Zhurnal, Khimiya. Moscow.

Refiner Nat. Gas. Mfr. Refiner and Natural Gasoline Manufacturer Houston. Texas.

Reichsarbeitsblatt.

Rend. Accad. Sci. Napoli. Rendiconti dell'Academia delle Scienze de Napoli. Naples.

Rep. Agr. Dept. Bengal. Reports of the Agricultural Department. Bengal.

Rep. Assoc. Hawaiian Sugar Tech. 11th. Ann. Meeting. Reports of the Association of Hawaiian Sugar Technologists. 11th Annual Meeting.

Rep. Govern. Sugar, Expt. Sta. Report of the Government Sugar Experiment Station, Tainan, Formosa.

Rep. Govt. Chem. Ind. Res. Inst. Reports of the Government Chemical Industrial Research Institute, Tokyo.

Rep. Ind. Res. Inst. Osaka Pref. Reports of Industrial Research Institute, Osaka Prefecture. Osaka.

Rep. New Engl. Assoc. Chem. Teachers. Report of the New England Association of Chemistry Teachers. New England.

Rep. N.R.L. Report of N.R.L. Washington.

Rep. Osaka Imp. Ind. Res. Inst. Japan. Reports of the Osaka Imperial Industrial Research Institute. Japan.

Rep. Osaka Prefect. Ind. Res. Inst. Reports of the Osaka Prefecture, Industrial Research Institute. Japan.

Répert. Pharm. Répertoire de Pharmacie. Paris.

Reprint Indian Assoc. Cultiv. Sci. Reprint Indian Association for the Cultivation of Science.

Rep. Sci. Res. Inst. Tokyo. Reports of the Scientific Research Institute.

Reps. Soc. Chem. Ind. on Prog. Appl. Chem. Reports of the Society of Chemical Industry on Progress in Applied Chemistry.

Repts. Govt. Chem. Ind. Research Inst. Tokyo. Reports of the Government Chemical Industrial Research Institute, Tokyo.

Repts. Himeji Inst. Technol. Reports Himeji Institute Technology. Himeji.

Repts. Liberal Arts Fac., Shizuoka Univ. Nat. Sci. Reports of the Liberal Arts Faculty, Shizuoka University, Natural Science. Japan.

Rept. Taiwan Sugar Expt. Sta. Report of the Taiwan Sugar Experiment Station. China.

Res. Bull. East Panjab Univ. Research Bulletin of the East Panjab University. India.

Res. Bull. Gifu Coll. Agr. Japan. Research Bulletin of the Gifu Imperial College of Agriculture. Japan.

Res. Bull. Panjab Univ. Research Bulletin of the Panjab University. India.

Res. Bull. Taiwan Fertiliser Co. Research Bulletin of the Taiwan Fertiliser Company. China.

Res. Rep. Nagoya Ind. Sci. Res. Inst. Research Reports of the Nagoya Industrial Science Research Institute.

Retorts. Brazil.

Rev. Agr. Maurice. Revue agricole et sucriere de l'ile Maurice. Mauritius.

Rev. Brasil Farm. Revista Brasileira de Farmacia. Brazil.

Rev. Centro estudiantes Farm. Bioquim. Revista del centro estudiente de farmacia y bioquimica. U.N.M.S.M. Buenos Aires.

Rev. Centro estud. Ing. Quim., Univ. Nacl. Litoral. Revista del centro estudiantes ingenieria y quimica, University Nacionale Litoral. Buenos Aires.

Rev. Chim. Bucharest. Revista de chimie (Bucharest) Rumania.

Rev. d'Optique. Revue d'Optique. Paris.

Rev. Financiera, Salitre y Minas (Santiago). Revista Financiera, salitre y Minas. Santiago.

Rev. Gén. Elec. Revue Générale de l'electricite. Paris.

Rev. Géol. Revue de Géologie et des sciences connexes.

Rev. Mét. Revue de metallurgie. Paris.

Rev. Neurol. Revue Neurologique. Paris.

Rev. Plásticos (Madrid). Revista de plasticos. Madrid.

Rev. Real Acad. Cienc. Exact., Fis. y Nat. Madrid. Revista de la real academia de ciencias exactas, fisicas y naturales de Madrid. Madrid.

Rev. Soc. Brasil. Quim. Revista da Sociedade Brasileira de Quimica. Brazil.

Rev. Sud-Americana Endrocrinol. Immunol. Quimioterap. Revista Sud-Americana de Endocrinologia, Immunologia, Quimioterapia. South America.

Rev. Tech. Luxembourg. Revue Technique Luxenboureòise. Luxemburg.

Reyon, Synthetica, Zellwolle. Frankfurt-am-Main.

Riv. Combustibli. Rivista dei Combustibli. Milan.

Riv. Ecol. Rivista di ecologia.

Rock Products. Chicago. Illinois.

Rubber Age N.Y. New York.

Rubber India. Bombay. India.

Russa.

S. Afr. J. Ind. South African Journal of Industries and Labour Gazette.

S. Afr. J. Med. Sci. South African Journal of Medical Sciences. Johannesburg. Union of South Africa.

S. Car. Agr. Expt. Sta. Circ. South Carolina Agricultural Experiment Station, Chemson Agricultural College, Circular.

Sbornik Nauch. Trudov Kuĭkyshev. Ind. Inst. Sbornik Nauchnykh Trudov Kuĭkyshevskii Industrial'nyi Institut imeni V.V. Kuĭkysheva. Kuĭkyshev. U.S.S.R.

Sbornik Rabot Radiatsiennoĭ Khim. Akad. Nauk S.S.S.R. Sbornik Rabot po Radiatsiennoĭ Khimii, Akademiya Nauk S.S.S.R. Moscow.

Sbornik Stateĭ Obshcheĭ Khim. Akad. Nauk S.S.S.R. Sbornik Stateĭ po Obshcheĭ Khimii, Akademiya Nauk S.S.S.R. Moscow.

Sbornik Trudov, Respub. Nauch.-Issledov. Inst. Mest. Stroitel. Mat. Sbornik Trudov, Respublikanskii Nauchno-Issledovatel'skii Institut Mestnykh Stroitel'nykh Materialov. Moscow.

Scand. J. Clin. Lab. Invest. Scandinavian Journal of Clinical and Laboratory Investigations. Oslo.

Schlögel u. Eisen. Schlögel und Eisen.

Schwefel und Stickstoff Studien.

School Sci. Rev. School Science Review. London.

Schriften zentral. biochim. Forschungs-Inst. Nahr.-Genussmittelind. U.S.S.R. Schriften des zentralen biochemischen Forschungs-Instituts der Nahrungs und Genussmittelindustrie. U.S.S.R.

Schrift. Königsberger Gelehrten-Ges. Schriften der königsberger Gelehrten-Gesellschaft.

Schr. Mineralog.-Petrog. Inst. Univ. Kiel. Schriften der Mineralgische und Petrographische Institut Universitat Kiel. Germany.

Schweits. Leder-Industrie Ztg. Halle aux Aurs. Schweitzer Leder-Industrie Zeitung, Halle aux Aurs. Switzerland.

Sci. Rep. Imp. Inst. Agr. Res. Pusa. Science Report of the Imperial Institute of Agricultural Research. Pusa.

Sci. Rep. Res. Inst., Tohoku Univ. Science Reports of the Research Institutes, Tohoku University. Sendai. Japan.

Science, China.

Science & Crime Detection. Japan.

Science and Culture, India. Calcutta.

Science, Japan. Tokyo.

Science et Inds. Phot. Science et Industries Photographiques. Paris.

Science of Light, Japan.

Scottish J. Agr. The Scottish Journal of Agriculture, Edinburgh.

Shoe Leather Rept. Shoe and Leather Reporter. Boston. Massachusetts.

Silicates Ind. Silicates Industriels. Brussels. Belgium.

Silikat Tech. Silikat Technik. Germany. N.Y.

Sitz. Akad. Wiss. Wien, Math.-naturw. Klasse. Sitzungsberichte der Akademie der Wissenschaften in Wien, Mathematisch-naturwissenschaftliche Klasse.

Sitz. Deut. Akad. Wiss. Berlin, Kl. Math.-Maturw. Sitzungsberichte der Deutschen Akademie der Wissenschaften zu Berlin, Klasse fur Mathematik und allgemeine Naturwissenschaften. Berlin.

Sitz. Math.-Naturw. Abt. Bayer. Akad. Wiss. Munchen. Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Abteilung der Bayerischen Akademie der Wissenschaften zu Munchen. Munich. Germany.

Sitz. Phys.-Med. Societät Erlangen. Sitzungsberichte der Physikalisch-Medizinischen Sozietät zu Erlangen. Germany.

Sklarské Pozhledy.

Soap. New York.

Soap and Chem. Specialties. Soap and Chemical Specialties. N.Y.

Socker Handl.

Soc. Roy. Belge Ing. et Ind. mém. Société Royale Belge des Ingénieurs et des Industriels. Mémoires. Brussels. Belgium.

Soda and Chlorine.

Soil Sci. Soc. Amer. Proc. Soil Science Society of America, Proceedings Wisconsin.

Soil Sci. Soc. Florida Proc. Soil Science Society of Florida Proceedings. Gainesville. Florida.

Soobshcheniya Akad. Nauk Gruzin S.S.R. Soobshcheniya Akademii Nauk Gruzin S.S.R. Tiflis. U.S.S.R.

Soobshcheniya Nauch. Rabot. Vsesoyuz. Khim. Obshchestva im Mendeleeva. Soobshcheniya Nauchnykh Raboty Vsesoyuznyi Khimii Obshchestva im Mendeleev. U.S.S.R.

Southern Power and Ind. Southern Power and Industry. Atlanta.

Sovet. Geol. Sovetskaya Geologiya. Moscow.

Sprawozdania Posiedzen Towarz. Nauk. Warsaw. Cl. Sprawozdania Posiedzen Towarzystwa Naukowego Warszawskiego. Classe.

Stand. Meth. Chem. Anal. Standard Methods of Chemical Analysis. New York.

Steel. Cleveland. Ohio.

Steklo i Keram. Steklo i Keramika. Moscow.

Stroitel. Prom. Stroitel'naya Promyshlennost. Moscos.

Sugar Bull. Sugar Bulletin. New Orleans.

Sugar Ind. Abstr. Sugar Industry Abstracts. Kent.

Sugar News.

Superphosphat. Das Superphosphat.

Svensk. Forskningsinst. Cement Betong Vid Kgl. Tek. Högskol. Stockholm, Handl. Svenska Forskningsinstitutet för Cement och Betong vid Kungl. Tekniska Högskolan i Stockholm, Handlingar. Stockholm.

Svensk. Mosskulturför. Tid. Svenska Mosskulturföreningens Tidskrift. Stockholm Sweden.

Svensk. Vetens. Arkiv. Kemi. Arkiv för Kemi, utgivet av Kungl. Svenska Vetenskapsakademien, Stockholm.

Symposium on Radiation Chem. Moscow. Symposium on Radiation Chemistry. Moscow.

Tanso. Tokyo.

Tech. Chem. Papier u. Zellstoff Fabr. Das Papier, Zeitschrift fur die Erzeugung von Holzstoff, Zellstoff, Papier und Pappe. Darmstadt. Germany.

Tech. Eau. La technique de l'eau et de l'assainissement. Brussels.

Tech. Mitt. Krupp. Technische Mitteilungen Krupp. Essen. Germany.

Tech. Moderne. La Technique Moderne. Paris.

Techn. Rep. Osaka Univ. Technology Reports of the Osaka University. Osaka. Japan.

Tec. Ital. Tecnica Italiana. Trieste. Italy.

Tehnički Pregled. Zagreb. Yugoslavia.

Teintex. Paris.

Tek. Tid. Uppl. C. Teknisk Tidskrift. Upplaga C. Stockholm.

Tekstil. Prom. Tekstil'naya Promyshlennost. Moscow.

Textile Bull. Textile Bulletin. Charlotte, N.C.

Textile Colorist. New York.

Textil-Praxis. Stuttgart. Germany.

Textile Rec. Textile Recorder. Manchester.

Textile Res. Textile Research. Princeton, N.J.

Tekstil-Rundschau. Switzerland.

Tids. Kjemi, Bergvesen Met. Tidskrift för Kjemi og Bergvesen og Metallurgi. Oslo.

Titanium Abs. Bull. Titanium Abstracts Bulletin. Washington.

Tohoku J. Exptl. Med. Tohoku Journal of Experimental Medicine. Tokyo.

Tonindustr. Ztg. u Keram. Rundschau. Tonindustrie-Zeitung und Keramische Rundschau. Berlin.

Toyo Rayon Shuho. Otsu. Japan.

Trans. Amer. Microscop. Soc. Transactions of the American Microscopical Society. Columbus. Ohio.

Trans. Canad. Inst. Min. Met. Eng. Transactions of the Canadian Institute of Mining and Metallurgy and Engineering. Quebec. Canada.

Trans. Ceram. Soc. Transactions of the British Ceramic Society. Stoke-on-Trent.

Trans. Edin. Geol. Soc. Transactions of the Edinburgh Geological Society. Edinburgh. Scotland.

Trans. Geol. Soc. Edinburgh. see *Trans. Edin. Geol. Soc.*

Trans. Geol. Soc. S. Africa. Transactions of the Geological Society of South Africa. Johannesburg.

Trans. Inst. Appl. Chem. U.S.S.R. Transactions of the Institute for Applied Chemistry U.S.S.R. Moscow.

Trans. Inst. Chem. Charkov Univ. Charkov University Transactions of the Institute of Chemistry.

Trans. Inst. Chem. Reagents, Moscow. Transactions of the Institution for Chemical Reagents, Moscow. Moscow.

Trans. Intern. Congr. Soil Sci. 4th Congr. Transactions of the International Congress of Soil Science. 4th Congress. Amsterdam.

Trans. VI Mendeleev Congr. Theoret. Appl. Chem. Transactions of the Mendeleev Congress of Theoretical and Applied Chemistry. 6th Congress. Kharkov.

Trans. Kentucky Acad. Sci. Transactions of the Kentucky Academy of Science. Louisville, Kentucky.

Trans. R. Inst. Appl. Chem. U.S.S.R. Transactions of the R. Institute of Applied Chemistry, U.S.S.R. Moscow.

Trans. Roy. Soc. Transactions of the Royal Society. London.

Trans. Sci. Chem. Pharm. Inst. Moscow. Transactions of the Scientific Chemical-Pharmaceutical Institute U.S.S.R. Moscow.

Trans. Sci. Inst. Fert. Insectofungicides U.S.S.R. Transactions of the Scientific Institute of Fertilizers and Insectofungicides. U.S.S.R.

Trans. Sci. Soc. China. Transactions of the Science Society of China. Taiwan. China.

Trans. Wisconsin Acad. Sci. Transactions of the Wisconsin Academy of Science, Arts and Letters. Madison, Wisconsin.

Trav. Congr. Jubilaire Mendeleev, Leningrad. Travaux du Congrès Jubilaire Mendeleev, Leningrad. U.S.S.R.

Trav. Inst. Lomonossoff Géochim. Crist. Minéral. Travaux de l'institut Lomonossoff de Géochemie, Cristallographie et Minéralogie. U.R.S.S.

Trav. Membres Soc. Chim. Biol. Travaux des Membres de la Société de Chimie Biologique.

Trav. Soc. Pharm. Montpellier. Travaux de la Société de pharmacie de Montpellier. France.

Trop. Agr. Ceylon. The Tropical Agriculturist. Ceylon.

Trudy Belorus. Sel'skokhoz. Akad. Trudy Belorusskoi Sel'skokhozyaistvennoi Akademii. Gorki, U.S.S.R.

Trudy Fiz.-Tekh. Inst. Akad. Nauk. U.S.S.R. Trudy Fiziko-Tekhnicheskogo Instituta, Akademiya Nauk Usbekskoi S.S.R. Moscow.

Trudy Inst. Fiz. Khim. Akad. Nauk S.S.S.R. 2, Issledovaniya po Korozii Metal. Trudy Instituta Fizicheskoi Khimii, Akademiya Nauk S.S.S.R. 2, Issledovaniya po Korozii Metal. Moscow.

Trudy Inst. Khim. Akad. Nauk U.S.S.R. Trudy Instituta Khimii, Akademiya Nauk Uzbekskoi S.S.R. Moscow.

Trudy Inst. Khim. Akad. Nauk U.S.S.R. Inst. Khim. Trudy Instituta Khimii, Akademiya Nauk Uzbekskoi S.S.R., Instituta Khimii. Moscow.

Trudy Kharkov. Khim.-Tekhnol. Inst. Im. G.M. Kirova. see *Trudy Kharkov.* Trudy Kharkovskogo Khimii-Tekhnologii Instituta Imeni G.M. Kirova. Kharkov, U.S.S.R.

Trudy Khim. Inst., Kirgiz. Filial Akad. Nauk S.S.S.R. Trudy Khimicheskogo Instituta, Kirgizskii Filial Akademii Nauk S.S.S.R. Moscow.

Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R., Otdel. Khim. Nauk. Trudy Komissii po Analiticheskoi Khimii, Akademiya Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk. Moscow.

Trudy Lab. Gidrogeol. Problem, Im. F.P. Savarenskogo. Trudy Laboratorii Gidrogeologicheskikh Problem Imeni Akademiya F.P. Savarenskogo, Akademiya Nauk S.S.S.R. Moscow.

Trudy Moskov. Inst. Tonkoi Khim. Tekhnol. Trudy Moskovskogo Instituta Tonkoi Khimicheskoi Tekhnologii imeni M.V. Lomonosova. Moscow.

Trudy Nauch.-Issledovatel. Inst. Khim., Khar'kov. Univ. Trudy Nauchno-Issledovatel'skogo Instituta Khimicheskogo, Kharkov University. Kharkov.

Trudy Sredneaziat. Univ. Khim. Nauk. Trudy Sredneaziatskogo Universiteta Khimicheskie Nauki. Uzbek S.S.R.

Trudy Ural. Ind. Inst. Kirova. Trudy Ural'skogo Industrial'nogo Instituta imeni S.M. Kirova. U.S.S.R.

Tsement. Leningrad. U.S.S.R.

Uchen. Zapiski Beloruss. Univ. Uchenye Zapiski, Belorusskii Gosudarstvennyi Universitet imeni V.I. Lenina. U.S.S.R.

Udobrenie i Urozhai (Fertilizers and Crops). Moscow.

Ukrain. Akad. Nauk Inst. Khim., Sbornik Trudov Pervoi Vsesoyuznoi Konferentzii (Neuprown) Rastvaram. Ukrainskii Akademii Nauk Institut Khimicheskii, Sbornik Trudov Pervoi Vsesoyuznoi Konferentzii (Neuprown) Rastvaram. Kiev. Ukr. S.S.R.

Ukrain. Fiz. Zhur. Ukrains'kii Fizichnii Zhurnal. Kiev. Ukr. S.S.R.

Ukrain. Khem. Zhur. Ukrains'kii Khemichnii Zhurnal. Kharkov.

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Union des Soc. Ind. France Troisième Congrès, Mulhouse. Union Internationale des Sociétés de Chimistes des Industries du Cuir, Troisième Congrès, Mulhouse. France.

Union S. Africa, Dept. Agr. Sci. Bull. Union of South Africa, Department of Agriculture, Science Bulletin. Pretoria. Union of South Africa.

Univ. Arizona Bull. University of Arizona Bulletin. Tucson. Arizona.

Univ. Chile, Fac. Quim. y Farm., Tesis Quim. Farm. Universidad de Chile, Facultad de Quimica y Farmacia, Tesis de Quimicos Farmaceuticos. Santiago. Chile.

Univ. Ill. Bull., Eng. Expt. Sta., Bull. Ser. University of Illinois Bulletin including Engineering Experiment Station, Bulletin Series. Urbana, Illinois.

Univ. Pittsburgh Bull. University of Pittsburgh Bulletin. Pittsburgh.

Univ. Studi Trieste, Fac. Sci., Ist. Chim. Universita degli Studi di Trieste, Facolta di Scienze, Istituto di Chimica. Trieste. Italy.

Urol. Cutaneous Rev. Uralogic and Cutaneous Review.

U.S. Atomic Energy Comm. United States Atomic Energy Commission. Washington.

U.S. Atomic Energy Comm. Nat. Sci. Found. Washington D.C. United States Atomic Energy Commission. Natural Science. Washington. D.C.

U.S. Bur. Mines, Rep. Invest. United States Bureau of Mines, Report of Investigations. Washington.

U.S. Bur. Stand. J. Res. United States Bureau of Standards, Journal of Research. Washington.

U.S. Dept. Agr. Bull. United States Department of Agriculture Bulletin. Washington.

U.S. Nat. Bur. Stand. Circ. United States National Bureau of Standards. Circulars. Washington.

U.S.S.R. State Inst. Tobacco Invest Bull. U.S.S.R. State Institute of Tobacco Investigation Bulletin. (Moscow).

Vegyi Ipar.

Verhl. Opt. Inst. Leningrad. Verhandlungen der Optische Institut, Leningrad.

Verre. Le Verre. Paris.

Verslag. Landb. Onderzoek. Rykslandbouwproefsta. Verslagen van Landbouwkundige Onderzoekingen Rykslandbouwproefsta. The Hague.

Vestnik Akad. Nauk Kazakh S.S.R. Vestnik Akademii Nauk Kazakhskoi S.S.R.

Vestnik Inzhenerov i Tekh. Vestnik Inzhenerov i Tekhnikov. U.S.S.R.

Vestnik Mashinostroeniya. Moscow.

Vestnik Moskov. Univ. Ser. Fiz.-Mat. i Estestver. Nauk. Vestnik Moskovskogo Universiteta Seriya Fiziko-Matematecheskikh i Estestvennykh Nauk.

Vestnik ustredniho Jednoty Reparu Ceskoslovenische. Prague.

Vestnik ustred. ustavu geol. Vestnik ustredniho ustavu geologickeho. Prague.

Vide. Paris.

Vitaminforsch. Vitaminforschung.

Vom Wasser. Weinheim. Germany.

Vostochnaya Neft.

W. Virginia Eng. Expt. Sta. Tech. Bull. West Virginia Engineering Experiment Station, Technical Bulletin. Morgantown. West Virginia.

Waseda Appl. Chem. Soc. Bull. Waseda Appl. Chemical Society Bulletin. Waseda.

Wasser, see *Vom Wasser.*

Water Pollution Abst., Dept. Sci. Ind. Research (Brit.) Water Pollution Abstracts, Department of Scientific and Industrial Research. London.

Water and Sewage Works. Chicago.

Water and Water Eng. Water and Water Engineering. London.

Werkstoffe u. Korrosion. Werkstoffe und Korrosion, Weinheim. Germany.

West of Scot. Agr. Col. Ann. Rep. West of Scotland Agricultural College, Annual Report. Glasgow.

West Va. Univ. Tech. Bull. West Virginia University, Technical Bulletin. Morgantown. West Va.

Wiadsmosci Institut Metals and Metallography.

Wien. Arch. Inn. Med. Wiener Archiv für innere Medizin und deren Grenzgekiele. Vienna.

Wien. Klin. Wochschr. Wiener Klinische Wochenschrift. Vienna.

Wisconsin Engr. Wisconsin Engineer. Madison. Wisconsin.

Wollen- u. Leinen-Ind. Wollen- und Leinen-Industrie.

Wood Inds. Wood Industries. London.

World's Paper Trade Rev. World's Paper Trade Review. London.

Yushi Kagaku Kykaishi. Japan.

Z. Astrophys. Zeitschrift für Astrophysik. Heidelberg. Germany.

Z. Berg.- Hütten- u. Salinenwesen preuss. Staat. Zeitschrift für das Berg-. Hütten- und Salinenwesen preussischen Staat.

Z. ges Giesserei-Praxis. Das Metall. Zeitschrift für das gesamte Giesserei-Praxis. Das Metall. Berlin.

Z. ges. Textil-Ind. Zeitschrift für die gesamte Textil-Industrie Dusseldorf. Germany.

Z. Immunitäts. Zeitschrift für Immunitätsforschung und experimentelle therapie. Stuttgart. Germany.

Zeitschrift für Landwirtschaftlichen Kammerprozess Braunschweig. Leipzig.

Z. Lebens. Untersuch. u. Forsch. Zeitschrift für Lebensmittel-Untersuchung und Forschung. Munich.

Z. phys. Chem. (Frankfurt). Zeitschrift für physikalische Chemie. Frankfurt.

Z. prakt. Geol. Zeitschrift für praktische Geologie mit besonderer Berucksichtigung der Lagerstattenkunde.

Z. Stomat. Zeitschrift für Stomatologie.

Z. Zuckerind. Bohmen Mahren. Zeitschrift für die Zuckerindustrie in Bohmen-Mahren.

Za Ekon. Topliva. Za Ekonomiya Topliva.

Zashchitnye Plenki na Solyakh, Akad. Nauk S.S.S.R. Zashchitnye Plenki na Solyakh, Akademiya Nauk S.S.S.R. Moscow.

Zastita Materiyale. Belgrade. Yugoslavia.

Zellstoff u. Papier. Zellstoff und Papier. Frankfurt. Germany.

Zemledelie. Moscow. U.S.S.R.

Zhur. Eksptl. i Teoret. Fiz. Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki. Moscow or Leningrad.

Zhur. Neorg. Khim. Zhurnal Neorganischeskoi Khimii. Moscow.

Zhur. Obshchei Khim. Zhurnal Obshchei Khimii. Moscow.

Zhur. Sakharnoi Prom. Zhurnal Sakharnoi Promyshlennosti. Moscow.

Zhur. Tekh. Fiz. Zhurnal Tekhnicheskoi Fiziki. Moscow.

Zink, Tech. Ber. Zink, Technische Berichte.

CHAPTER I

LITHIUM

SECTION I

THE OCCURRENCE OF LITHIUM

By P. C. L. THORNE and K. W. ALLEN

Spectroscopic evidence indicates that lithium in the sun[1,2] may be largely present as the isotope ^7Li.[1] The element has also been detected in the spectra of T Tauri[3] and R Andromedae[4] and in carbon stars.[5] The number of lithium atoms in interstellar space is estimated[6] to be not more than 5×10^{-11} per c.c. The mean content of lithium in the earth's crust is estimated[7] to be 4×10^{-5}% while the abundance of lithium has also been estimated in cosmic radiation.[8] The average content of igneous rocks[9] is given as 0·014% Li_2O, while that of sedimentary rocks is 0·011%, in agreement with the geochemical cycle. The amount of lithium in sea water has been variously stated as 0·26 mg. per kg.[9] and 0·1 mg. per l.[10] The wide terrestrial distribution of lithium in relatively small quantities[11-15] is reflected in general surveys of mineral products. The minimum lithium content for economic exploitation is said[16] to be 3·5%.

The content of lithium in mineral springs in France and French possessions has been investigated by R. Bossuet[17-19] while other workers have investigated Japanese springs.[20-22] The element is also present in springs in Konya Province, Turkey, (0·36 g. LiCl/l.),[23] and Parkent (Uzbekistan) (0·9 mg. Li/l.),[24] in waters from the Turin Hills (0·01 g. Li_2O/l.)[25] and in the waters of Mondovi Lurisio (0·01–0·05 mg. Li_2O/l.),[26] and a few other places[27,28] besides the sources reported in earlier years. The brine from Searle's Lake (California) contains 0·033% of lithium chloride, the element appearing as a scale of dilithium sodium phosphate, Li_2NaPO_4, in the evaporators on concentration.[29,30] A rich source of lithium is the drainage water from the Sierra Almagrera mines[31] which contains 0·33 g. LiCl per l. It is said that from this source 3300 kg. of lithium chloride flows into the ocean per day.

The geochemistry of the formation of lithium minerals, with special reference to the Li:Mg ratio and the correlation between this and the Mn:Fe ratio, has been investigated in the Swedish deposits.[32] Variations in, *inter alia*, lithium concentrations have also been used in considering the origin of igneous rocks[33] and the use of variations in isotope ratios has been reviewed[34] with special reference to natural waters. The pegmatites of California have been studied[35] and the origin of the lithium in them has been investigated. South Dakota pegmatites have been reviewed[37] and one of them has yielded a flotation concentrate of spodumene containing 5·93% Li_2O.[38] The pegmatites in Colorado, Wyoming and Utah have been examined for lithium and this source has already been exploited.[39,40] Analyses of the Norwegian pegmatites and other lithium-bearing minerals show that many of these rocks contain more than 3% Li_2O.[41-43] In France[44,45] the production from the deposits of lepidolite at Ambazac (4% Li) and from those of amblygonite at Montebras (8·40% Li_2O) is sufficient to supply the French industries. Some lithium is found in spodumene (5·55% Li_2O) occurring at Lalin in Galizia (Spain)[46] and in the leucite of Monte Somma (Italy),[47] but the extensive lepidolite deposits 'Rozna' in Moravia (4·1% Li) constitute one of the most important sources of this element.[48-51] In the U.S.S.R., deposits of lithium minerals have been discovered in the North Caucasus region,[52,53] in the Ukraine[54] (with 6% Li_2O) at Altyn-Tau (with 7·54% Li_2O),[55] in E. Kazakhstan[56] in the Urals[57] and in other localities.[58] The rare lithium amphibole, holmquistite, has also been noted in Russia in gabbroanorthosite rocks. The crystals are columnar, 1·5-2 cm. long, with prismatic cleavage. They are bluish violet, of hardness 5-6, *d* 2·95, with characteristic pleochroism.[59] The occurrence of lithium in South Africa,[60-62] India,[63] Korea,[64] Japan[65] and U.S.A.[66-68] has been further explored: North Carolina spodumene may contain 6-7% Li_2O,[69] and that from Taos County, New Mexico, up to 10% Li_2O.[70] In Canada deposits containing up to 5% Li_2O are found in Quebec[71-74] and in Manitoba.[75-77] Although lithium minerals occur in Australia[78] there has been no production in recent years. Minerals containing lithium are also reported in various places, including Argentine,[79] Brazil[80] and Finland[81] as well as Scotland[83,84] and Northern Ireland.[85]

The presence of lithium in soils has been studied[86,87] and a content of 0·3 mg. per 100 g. is reported[88] as an average of 21 samples. In seeds[89] (40 species) the Li content is less than that of the rest of the plant and ranges from 0·01-0·13 mg. Li per kg. for cereals, and from 0·04-0·56 mg. per kg. for other species; while for cryptogams lithium is reported[90] in all samples examined, with an average value of 1 mg. Li per kg. dry material.

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SECTION II

THE PREPARATION AND USES OF LITHIUM

By J. P. QUIN

THE LABORATORY PREPARATION OF LITHIUM

In the original Treatise (Mellor,II,447) metallic lithium is described rather as a chemical curiosity. This is no longer true; lithium of over 97% purity is now sold commercially and this material, either as such or after purification, is usually considered to be suitable for all normal laboratory purposes. The fact that lithium has now become a common chemical substance readily available on the market may explain why comparatively little study has been devoted recently to methods of preparing the metal in the laboratory. Nevertheless, such methods as have been used for the formation and preparation of lithium during the last thirty-five years are here described. Analytical figures showing the purity of the lithium made by the various methods are given where such information is available.

The Formation and Preparation of Lithium by Chemical Reaction.

Lithium is the first member of the group of alkali metals, which includes sodium, potassium, rubidium, cæsium and the radioactive element francium. The chemical properties of the element differ in some ways from those of the other alkali metals, and the general methods of formation and preparation of the alkali metals by chemical means, as described under the preparation of sodium (see Sect. XXIII), are not always applicable to lithium. Although lithium is readily obtained by electrolytic methods, there are circumstances in which it may be preferable to prepare the metal by chemical reaction. In general it may be said that reactions whereby lithium is produced chemically involve either the thermal decomposition of lithium compounds or the reduction of lithium compounds with metallic or non-metallic reducing agents. These reactions are preferably carried out under reduced pressure and at such a temperature that the lithium produced is removed from the sphere of reaction in the form of vapour.[1] Unlike the other alkali metals, lithium combines readily with carbon to form a comparatively stable carbide, and on this account the use of carbon or carbides, such as calcium carbide, as reducing agents is not recommended.[2,3] As will be seen by reference to the appropriate sections dealing with the alkali metal compounds, the free energies of formation of lithium compounds tend to be more highly negative than those of the corresponding compounds of the other alkali metals and this, together with the low volatility of lithium, makes the preparation of lithium by thermal routes rather more difficult than that of the other alkali metals under similar conditions.[1]

Thermal Decomposition of Lithium Salts.

The alkali metals, with the exception of lithium, have been prepared by Suhrmann and Clusius by thermal decomposition of their respective azides in vacuo. These authors state, however, that as their experiments were carried out in glass apparatus, and as lithium even below its melting point attacks glass, they did not attempt the preparation of this metal.[4] Since lithium readily reacts with nitrogen to form lithium nitride, it is unlikely that the method could be successfully adopted for the preparation of the metal, and previous workers have found that lithium azide readily explodes on heating.[5] Small amounts of lithium have, however, been formed by the thermal decomposition of lithium ferrocyanide.[6]

Thermal Reduction of Lithium Compounds with Metallic and Non-Metallic Reducing Agents.

It has been claimed that for the preparation of small quantities of lithium (not exceeding a few grams) in the laboratory, thermochemical methods involving the reduction of a lithium compound with a suitable reducing agent may offer some advantages over electrolytic methods which are more suitable for the preparation of amounts of the order of several pounds.[7]

Lithium is formed when lithium oxide is reduced with aluminium at 1150°C.[8] Under reduced pressure, below 6 mm. mercury, the metal is liberated at 750–900°C.[9] The reduction of lithium oxide with aluminium in the presence of basic oxides is discussed below (see page 7). .

The preparation of lithium by reduction of lithium chloride with sodium is not satisfactory as the reaction quickly reaches an equilibrium and very little metallic lithium is produced.[14]

On a small laboratory scale lithium may conveniently be prepared by reducing lithium chloride with metallic barium.[7] Thus when barium in about 80% of the stoicheiometric requirement reacts with lithium chloride at about 850°C. at normal pressure in an inert atmosphere, lithium metal containing 5–8% of barium is obtained in about 85% yield, based on barium. Further treatment with a considerable excess of lithium chloride gives metal containing about 0·1% of barium, with total impurities amounting to 0·5%. Under these conditions the maximum yield of lithium obtained is 60%. Much of the loss of lithium is attributed to the difficulty in removing metal which is physically entrapped in the salt. The method has the advantage of avoiding the use of high vacuum and also of excessively high temperatures.

Lithium may be prepared by the Hackspill method whereby lithium compounds such as lithium chloride are reduced with calcium according to the equation:-

$$2LiCl + Ca \rightarrow CaCl_2 + 2Li.$$

A detailed description of the apparatus and the necessary procedure has been given.[10] Briefly, an intimate mixture of lithium chloride and calcium is heated in an evacuated tube when the lithium distils off and is condensed. For satisfactory results it is desirable to use an excess of calcium and the product so obtained is contaminated with about 3–4% of calcium. An excess of lithium chloride gives a dark coloured melt, which may contain a subchloride, and no lithium is obtained. Hackspill considers the method inferior to the Guntz electrolytic route to the metal, however, and does not recommend it for the preparation of lithium in the laboratory.

Lithium is not readily formed by reducing lithium compounds with iron and it has been found that when the reduction is carried out at low pressure, the lithium compounds tend to decompose or volatilize without reacting with the iron.[8,11,12]

Thus when lithium fluoride, previously dried in vacuo at 300°C., is heated under reduced pressure with excess of iron at about 1000°C., no reaction takes place. At 1200°C. the lithium fluoride volatilizes without reacting with the iron, and no lithium metal is formed. When mixtures of lithium chloride and iron are heated at 1000°C. in vacuo, the lithium chloride volatilizes unchanged and the iron is unattacked, and no lithium is formed when lithium chloride vapour is passed over iron in vacuo at 1360°C.[8] Lithium sulphate reacts with iron in vacuo at about 860°C., the melting point of the sulphate, to give a mixture of lithium oxide, ferrous and ferrosoferric oxides and iron sulphide, and no lithium is formed even when the temperature is raised to 1100°C.[8,12] Under similar conditions lithium nitrate reacts with iron at 300°C. with the formation of nitrous fumes. At a somewhat higher temperature the nitrous fumes are decomposed by iron with the formation of iron oxide and nitrogen. Reaction ceases when all the lithium nitrate has been reduced to lithium oxide, but no lithium metal is formed even when the temperature is raised to 1100°C. When lithium carbonate is heated with iron in vacuo, decomposition of the carbonate starts about its melting point, 700°C., and lithium oxide is formed, but the iron remains unattacked. Similarly when lithium hydroxide is heated with excess of iron in vacuo, evolution of hydrogen starts at about 500°C. and proceeds rapidly at 600°C. owing to the reaction:-

$$6LiOH + 2Fe \rightarrow 3Li_2O + Fe_2O_3 + 3H_2.$$

When, however, lithium oxide is heated with excess of iron in vacuo at temperatures over 1300°C. a product which consists of lithium metal much contaminated with lithium oxide distils off: this result is contrary to those obtained in previous work on the subject.[8] It has been found that lithium silicate, when reduced with iron at low pressure at 1300°C., reacts very similarly to lithium oxide, giving as the product lithium metal contaminated with oxide.[8] The preparation of lithium by the reduction of lithium sulphide with iron at high temperatures has been patented. The addition of lime or other basic oxides is recommended.[13]

Magnesium has been used to prepare lithium by the reduction of lithium compounds.[8,14] Lithium is formed when lithium oxide or hydroxide is heated with magnesium in vacuo at 550°C., but magnesium is considerably more volatile than lithium, and so tends to distil off preferentially from the reaction products.[8,14] The preparation of lithium by reducing lithium oxide with magnesium at pressures of less than 6 mm. of mercury at a temperature of 700-900°C. has, however, been the subject of a patent.[9] When mixtures of lithium oxide, calcium oxide and magnesium are pelleted and heated in vacuo, the product that distils off is not lithium, but a lithium-magnesium alloy containing about 50% of magnesium.[14]

Lithium compounds are not readily reduced by nickel.[8] Thus when lithium chloride is heated with excess of nickel at about 900°C. under reduced pressure, the chloride volatilizes unchanged and no lithium is formed. When lithium hydroxide is heated with nickel in vacuo, lithium oxide is produced with the evolution of water vapour which then reacts with the nickel to form nickel oxide and hydrogen. When all the lithium hydroxide is transformed into lithium oxide no further reaction takes place. Lithium nitrate reacts readily with nickel under similar conditions to give nickel oxide, lithium oxide and nitrogen, but no metallic lithium is formed.

Attention has recently been directed to the preparation of lithium by reducing lithium compounds at high temperatures and low pressures with silicon, ferrosilicon or aluminium, so that the lithium metal formed distils off and is recovered by condensation.[14,19] The reduction is preferably carried out in the presence of a basic oxide such as lime.[14] Thus lithium is produced[15] when mixtures of lithium oxide and calcium oxide are briquetted with a reducing agent such as silicon or aluminium, and then heated at temperatures of 950°-1000°C. under a pressure of less than 0·001 mm. The reduction proceeds according to the equations:-

$$(1)\ 3Li_2O + CaO + 2Al \rightarrow CaO,Al_2O_3 + 6Li$$

$$(2)\ 2Li_2O + 2CaO + Si \rightarrow 2CaO,SiO_2 + 4Li.$$

The calcium oxide is added so that it may combine with the alumina or silica formed by the reaction. About 10% excess of reducing agent above the stoicheiometric proportion is required, and briquetting is essential to ensure intimate contact between the reactants. Over 75% of the lithium content of the charge is recovered when silicon is used as reducing agent, and with aluminium the recovery exceeds 80%. The use of aluminium in the reduction has the further advantage that the reaction may be carried out at a slightly lower temperature.

It is claimed that the presence of sulphate, sulphite, silica, barium, calcium and appreciable amounts of iron in the raw materials does not give rise to any trouble in the thermal production of lithium.[14] These impurities are very deleterious when making the metal electrolytically. The lithium made by the thermal route is a highly pure metal containing 0•01% of silicon, 0•01% of aluminium and 0•04% of calcium. The lithium oxide used is prepared by calcining lithium carbonate in vacuo, but attempts to carry out calcination and reduction of the oxide in a single stage, by vacuum distillation of briquetted mixtures of lithium carbonate, calcium oxide and aluminium or silicon, were unsuccessful and no lithium was obtained.[15]

The production of metallic lithium from a mixture containing 50•06% of lithium hydroxide, 14•34% of lithium carbonate, and 35•11% of water by reduction with aluminium has been described.[15a] The mixture is heated at 800°C. under a reduced pressure of 0•09–0•01mm. of mercury to give a product containing 96•02% of lithium oxide and 1•45% of lithium carbonate. This product is then reduced with 200 mesh aluminium powder at 1000°C. under a reduced pressure of 0•04–0•001mm. of mercury.

The yield of lithium so obtained varies from 24•7 to 84%. The purity of the metal is described as high; magnesium, aluminium and sodium are present only in spectrographic traces.[15a]

It has been proposed to apply vacuum metallurgy methods to the production of lithium directly from its ores such as the silicate or phosphate.[16,17] Lithium-bearing salts from Searles Lake in the United States have also been successfully reduced by this method.[19] A briquetted mixture containing the powdered ore, excess of calcium oxide and a reducing agent such as aluminium, aluminium–silicon alloy, silicon or ferrosilicon, is heated at a temperature above 900°C., preferably at 1050–1150°C., under low pressure, less than 1 mm. of mercury and preferably between 0•001 and 0•1 mm. of mercury. With lithium ore which also contains sodium or potassium, the three metals vaporize successively in the order potassium–sodium–lithium and condense at different successively higher temperatures. The potassium and sodium can thus be recovered as useful by-products. In the recovery of lithium from its phosphate ores, phosphorus volatilizes before the alkali metals and condenses at a lower temperature. Yields of approximately 90% of the lithium content of the ore have been obtained.[16] When the reduction is carried out at a pressure of 0•025 mm. using powdered spodumene briquetted with excess of calcium oxide and silicon and aluminium, yields of approximately 90% are obtained, but the metal is less pure than that obtained by the electrolytic method.[18]

The preparation of lithium by reducing lithium halides with silicon has been attempted,[14] but when a briquetted mixture of lithium chloride, calcium oxide and silicon is heated in vacuo at 850°C., no lithium metal is formed but a considerable amount of lithium chloride is volatilized from the reaction mixture. When lithium fluoride is used in place of lithium chloride better results are obtained, contrary to the experience of previous workers who found that lithium was not formed by the reduction of lithium fluoride with silicon. A briquetted mixture of lithium fluoride, calcium oxide and silicon reacts at 1100°C. under reduced pressure according to the equation:-

$$4LiF + 4CaO + Si \rightarrow SiO_2,2CaO + 2CaF_2 + 4Li.$$

No silicon tetrafluoride is formed, but the lithium metal distilling off is contaminated with lithium fluoride. The recovery of lithium is 22•7%. When aluminium is used in place of silicon, the reaction proceeds at a temperature of 1000° C. according to the equation:-

$$6LiF + 4CaO + 2Al \rightarrow Al_2O_3,CaO + 3CaF_2 + 6Li.$$

The condensed lithium metal contains 90% lithium and 10% lithium fluoride and the recovery of lithium is 44·2%.[14]

Zirconium metal in powder form has been used as a reducing agent in the preparation of lithium from lithium salts.[20] When lithium chromate and zirconium powder in the proportion 1:2 and 1:4 are heated *in vacuo* at temperatures ranging from 450° to 600°C., reduction occurs with explosive violence and lithium is formed in a 60% yield. On the other hand a 1:8 mixture reacts smoothly and quietly under similar conditions, but the yield of lithium is small. This method of preparation is considered to be suitable for making small quantities of lithium in the laboratory.

ELECTROLYTIC METHODS OF PREPARATION

Lithium from Aqueous Solutions of Lithium Salts.

It has been proposed to prepare lithium by distilling a lithium amalgam, prepared by the electrolysis of an aqueous solution of a lithium compound in the presence of mercury. The mercury volatilizes, leaving a residue of lithium metal, which, however, is likely to be contaminated with small amounts of mercury.[21] The extraction of lithium from lithium amalgam by liquid ammonia has been patented.[21a]

Electrolysis of Solutions of Lithium Salts in Non-aqueous Solvents.

Small amounts of lithium have been obtained by electrolytic deposition from solutions of lithium salts in non-aqueous solvents, but such processes do not appear to be very satisfactory for the preparation of appreciable amounts of pure lithium in the laboratory. Lithium acetylide is soluble in liquid ammonia and behaves as a weak electrolyte comparable with silver cyanide. On electrolyzing such a solution, lithium is liberated at the cathode and produces a local coloration in the solution, while small amounts of gas and carbon appear at the anode.[22]

According to a patent lithium is prepared by the electrolysis of a non-aqueous liquid comprising anhydrous liquid ammonia, methylamine, ethylamine, pyridine or mixtures of these liquids, containing a lithium salt, as for example the perchlorate or thiocyanate. Inert conductors such as iron, copper or carbon are used as cathode and carbon is the preferred material for the anode. Depending on the concentration of salt in the anhydrous liquid, which should be at least 2g.-mol. per litre, the lithium may be deposited as a colloid, suspension, paste or massive metal. It is claimed that lithium may be obtained in a high degree of purity from the deposited metal by separating it from the electrolyte and evaporating the excess solvent which is substantially free from unelectrolyzed salt.[22a]

The electrolytic decomposition of lithium salts in nitrobenzene and other organic solvents has been studied.[23-25] Electrolysis of nitrobenzene solutions of complex lithium compounds, prepared by fusing mixtures of lithium bromide or chloride with aluminium bromide or chloride, deposits lithium metal at the cathode. The use of a low current density and a diaphragm increases the yield of the metal, which is obtained at about 35% current efficiency.[24] When, however, solutions of these lithium complex compounds in benzene are electrolyzed, no lithium is deposited.[23]

Electrolytic studies of solutions of aluminium bromide–lithium chloride and aluminium chloride–lithium chloride in a number of organic solvents have been carried out under various conditions of temperature and concentration.[25] Aluminium chloride–lithium chloride solutions in nitrobenzene have a higher conductivity than solutions of aluminium bromide–lithium chloride and so experiments tended to be confined to the former. In the electrolysis of aluminium chloride–lithium chloride solutions in nitrobenzene, the presence of xylene improves the nature of the deposit and also the yield of metal, but as it also reduces the conductivity it is desirable to operate with not more than 3% of xylene, which is the minimum amount necessary to affect deposition favourably. When a solution containing 10% of a mixture of 0·9 moles of lithium chloride with 1 mole of aluminium chloride, 3% of xylene and 87% of nitrobenzene is electrolyzed at a current density of 0·0004amp. per sq. in., lithium is obtained at a current efficiency of 36%. By stirring the solution during electrolysis the current efficiency is raised to 40%. During electrolysis the temperature rises considerably, but by maintaining the temperature at 0°C. the current efficiency may be increased to 64%. The deposited lithium, which is preferably removed from the cathode under the protection of an inert organic liquid, is of a powdery nature and does not readily coalesce even when heated to its melting point.

Electrodeposition from these complexes has also been attempted using a number of other organic solvents in place of nitrobenzene, but no satisfactory results were obtained.[25]

Lithium has been deposited by the electrolysis of lithium iodide dihydrate in nitrobenzene, using a platinum cathode. The quality of the metal was poor.[25a]

The electrolytic separation of lithium from solutions of lithium chloride and lithium nitrate in anhydrous pyridine has been studied,[26] electrolysis being carried out at various current densities up to 0·2amp. per dm.^{2} using a mercury cathode and a platinum anode. Pyridine containing 5–10% of water was found to give results differing completely from those obtained when using anhydrous pyridine, and this is attributed to the separation of lithium hydroxide when water is present.

More recent work on the preparation of lithium by the electrolysis of solutions of lithium salts in pyridine did not give very satisfactory results. Considerable difficulty was experienced in obtaining deposits of appreciable thickness that remained untarnished, and there appeared to be a reaction between lithium and pyridine. The problem of collecting a thin deposit of the metal from the electrode was also difficult, and the method is not recommended for the preparation of the metal.[27] Lithium has been deposited in an amorphous and impure form by electrolysis of (*a*) lithium bromide, (*b*) lithium iodide dihydrate in pyridine and in quinoline.[25a] Small quantities of impure lithium appear to be formed by the electrolysis of a 25% solution of lithium bromide in ethylenediamine at 100°C., using a copper cathode with an immersed area of 2 cm.^{2}, and a lithium amalgam anode located 1cm. from the cathode.[28] With a current of 0·02amp. a brown deposit, without metallic lustre, is obtained at the cathode; this deposit reacts violently with water or with alcohol evolving hydrogen and it is suggested that it contains free lithium metal.

The electrodeposition of lithium from solutions of lithium salts in fused alkyl pyridinium halides, which may be regarded as non-aqueous solvents, has been investigated.[24] A mixture of lithium chloride and fused ethyl pyridinium bromide was electrolyzed at voltages between 6 and 12V., using a platinum cathode and a carbon rod anode. The temperature of electrolysis was about 135°C.; under these conditions lithium chloride was found to be almost completely insoluble in the bath and attempts to deposit lithium metal were unsuccessful. Similar results were obtained using lithium sulphate and lithium nitrate in place of lithium chloride.

Electrolysis of Fused Lithium Compounds.

Lithium does not appear to have been made by the electrolysis of fused lithium hydroxide as sodium is made from sodium hydroxide in the Castner cell. It has been found that lithium reacts with molten lithium hydroxide to give lithium monoxide and hydrogen, and this reaction, which takes place readily at temperatures at which electrolysis of the hydroxide may be carried out, prevents the preparation of the metal in this way.[30] It is claimed, however, that the yield of lithium in the electrolysis of fused lithium hydroxide can be increased by adding to the molten electrolyte lithium bromide, iodide or chloride in the proportion of 25-eutectic mol.%, and maintaining the bath at a temperature not exceeding 450°C.[31]

Hackspill, who had carried out extensive researches on the thermal production of the alkali metals, stated in 1928 that in his opinion no chemical method could hope to rival the electrolysis of fused lithium chloride melts for the preparation of lithium in the laboratory, and it is probable that this is equally true today for quantities exceeding a few grams.[1] In an electrolytic process the current efficiency is influenced by the solubility of the liberated metal in the electrolyte, and the solubility of lithium in fused lithium chloride has been discussed.[32]

Lithium has been prepared by the electrolysis of fused lithium chloride at 640°C. The cell operated at 4·6V. and a current density of 2-3amp./cm.^{2} The current efficiency was 68·4% and the energy efficiency 20kWh./kg. of lithium. The total time of electrolysis was approximately 3hr.[32a]

According to Guntz, lithium may be prepared very conveniently by electrolyzing a fused mixture of equal parts of lithium chloride and potassium chloride in a porcelain crucible (Mellor, II, 449).[33] The solubility of lithium in pure fused lithium chloride is high,[32] and the addition of potassium chloride to give an electrolyte which can operate at a lower temperature is likely to be beneficial. The melting point of the preferred bath is about 450°C. In one preparation an iron cathode and a carbon anode are used, and it is said that the cell does not require a diaphragm. The cell operates at 10amp. and 20V. and the product is 98-99% lithium containing 1-2% of potassium.[1]

In a modified form of the Guntz method, electrolysis is carried out in a heat-resistant steel container, heated by either gas or electricity, using a stainless steel cathode and a carbon anode.[34] It is claimed that by careful regulation of the operating conditions lithium containing only small quantities of potassium can be produced. It is, however, not possible to obtain lithium entirely free from potassium.[34a] In order to make sodium-free lithium, however, it is necessary to use an electrolyte free from sodium compounds. It is said that the electrolysis of fused mixtures of sodium chloride and lithium chloride does not yield a satisfactory product:[27] the decomposition voltage of sodium chloride is lower than that of potassium chloride, and this would result in the lithium containing larger amounts of impurity.

.The preparation of small quantities of pure lithium by the electrolysis of molten lithium chloride of high purity has been described.[35] The electrolysis is carried out in a nickel crucible, with an Acheson graphite anode and an iron wire with a loop in the end for a cathode. The electrodes are separated by a partition of quartz instead of the usual asbestos board which was found to introduce impurities into the metal. The lithium chloride used in the preparation was found on spectroscopic test to contain a trace of sodium, together with smaller traces of iron, magnesium and calcium: the lithium produced on electrolysis showed, however, only a trace of sodium, the other impurities being eliminated.

The development of a miniature cell for the preparation of lithium from small amounts of lithium chloride has been described.[27] The electrolysis is carried out in a graphite container which acts as anode, using an alundum diaphragm and a stainless steel cathode. The charge is 35-40g. of lithium chloride and the yield of metal readily available is about 40% of the lithium content of the chloride; this may be increased by continued operation, at decreased efficiency. The method is recommended for the conversion of small quantities of lithium isotope compounds into lithium metal,[27] but no figures are given for the purity of the product.

It is claimed that lithium of high purity is obtained when the electrolysis is carried out in a fused bath consisting of 85–90% of lithium bromide and 10–15% of lithium chloride (Mellor, II, 449). The lithium metal made in this way was found, however, to contain 0·17% of sodium, and for many purposes this is deleterious.[36] This sodium presumably came from the lithium salts used in the electrolysis and the use of pure raw materials might be expected to yield lithium substantially free from sodium.

The electrolytic mobility of ^{6}Li in molten lithium chloride is greater by 2·2% than that of ^{7}Li, and concentrates of these isotopes have been prepared by electrolysis of the fused salt.[36a,b]

The decomposition of other lithium compounds by electrolysis has also been attempted. Thus, when fused lithium hydride is electrolyzed lithium metal is deposited at the cathode and hydrogen is set free at the anode. It is interesting to note that hydrogen is here an anion, whereas in the electrolysis of water and acids and in almost all other cases, hydrogen appears at the cathode.[37-40]

The electrolysis of fused lithium hydride has been shown to obey Faraday's law. Lithium hydride can also be electrolyzed in the solid state at temperatures much below its melting point. Thus, experiments carried out at temperatures ranging from 550° to 650°C., with a current of 2amp. at 10V., gave approximately quantitative results as measured by hydrogen evolution, though efficiencies tended to fall rapidly on continued electrolysis. The metallic lithium formed at the cathode was invariably contaminated with lithium hydride, and analysis of the product showed percentages of metallic lithium varying from 55 to 74%.[39]

There are indications that a fused melt of lithium hydride can act as an ionizing solvent and in such circumstances it may be possible to bring about the electrical decomposition of a dissolved lithium compound. Thus, for example, lithium carbide is soluble in fused lithium hydride, and when this solution is electrolyzed carbon is deposited at the anode. It is believed that this is not due to the action of hydrogen on the carbide as this can occur only at temperatures above those at which the electrolysis is carried out, and it is concluded that the carbide is ionized in the molten hydride. In these circumstances lithium should be deposited on the cathode.[40,41]

Electrolysis of Fused Salts in the Presence of a Molten Metal Cathode.

A recent patent claims the production of highly pure lithium by electrolysis of a fused lithium salt in the presence of a molten metal cathode in which lithium is soluble, followed by recovery of lithium by distilling the enriched cathode metal under reduced pressure.[42] Thus, a lithium-copper-aluminium alloy is prepared by electrolyzing a fused mixture of potassium and lithium chlorides using a 50% copper-50% aluminium alloy as a molten cathode, with a graphite anode. The cell operates at 250amp. and 5V. with a working temperature of about 750°C., and an alloy containing 4·2wt.-% (equivalent to 19·4 atomic-%) of lithium is obtained. On distilling this alloy under reduced pressure at about 870°C. the lithium content of the alloy is reduced to 0·18%. This residual lithium-copper aluminium alloy is then returned to the cell for further enrichment by electrolysis. The lithium metal obtained in the distillation is said to be of high purity. It contains 0·15% of potassium, 0·08% of calcium and 0·08% of aluminium.

A number of other alloys have been tried in place of copper-aluminium as a molten cathode. Magnesium is considered to show some promise, but the lithium content is limited to 2·4% for satisfactory working. Moreover, distillation of the lithium-magnesium alloy so prepared is said to present some difficulty.

Lithium Alloys by Electrolysis.

The solution of lithium metal in liquid ammonia, obtained by the electrolysis of a lithium salt in that solvent, may be used in the preparation of lithium alloys. Thus, for example, lithium plumbide can be prepared by reacting lead with the solution, and subsequently removing the ammonia by evaporation.[42a]

Lithium-barium-lead alloys have been prepared by the electrolysis of fused mixtures of lithium and barium chlorides in the presence of a molten lead cathode at 800°-900° C.[43] The preparation of lithium-copper-aluminium by electrolysis has been described above.

Theoretical aspects of the electrolysis of fused lithium salts have been discussed,[44] and phase diagrams have been given for fused lithium salts which may be used in the electrolytic preparation of the metal.[45] The preparation of lithium alloys is also discussed later (see page 19).

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THE INDUSTRIAL PREPARATION OF LITHIUM

Lithium was first produced in appreciable quantities in 1854 by Bunsen and Matthiessen, who obtained the metal by the electrolysis of fused lithium chloride.[1] In 1893 Guntz found that the electrolysis was considerably simplified by using as electrolyte a fused mixture of lithium chloride and potassium chloride, and this bath has been used for the production of the metal on the commercial scale ever since.[2]

Lithium ores are relatively plentiful and not unduly expensive, and the preparation of the metal offers little difficulty. Moreover, lithium is the least reactive of the alkali metals and is not dangerous to handle. Nevertheless, until about thirty years ago, the metal was regarded as a chemical curiosity, and it is significant that the original Treatise, when enumerating uses for the alkali metals, did not mention a single laboratory or industrial application for lithium.

During the 1914–1919 war the Metallgesellschaft A.G. of Frankfurt, Germany, developed an aluminium-zinc alloy containing about 0·1% of lithium. Shortly after the war, the Metallgesellschaft produced an alkali hardened lead-base bearing alloy in which lithium played an essential part. These alloys were the first major industrial application of lithium and led to the production of the metal on the commercial scale in Germany.

In the United States, the manufacture of lithium by electrolysis was started a few years later,[3] and in the period 1930–1940 the world output of the metal so increased that lithium became second in importance to sodium in alkali metal production.[3] During the 1939–1945 war substantial amounts of lithium were made for the manufacture of lithium hydride which was used on an extensive scale as a convenient source of hydrogen for military purposes.[3] The lithium output in the U.S.A. in 1953 was 35 short tons. This does not include metal used in the hydrogen bomb project.[4a] The maximum lithium metal capacity for 1955 in the U.S.A. is estimated to be about 200 short tons. This is probably 85% of the world production capacity.[4b,c] No recent figures for world production are available. Several of the reviews on the production of lithium metal give extensive bibliographies.[2-6,5-14d,20]

The Manufacture of Lithium by Chemical Processes.

Attention has recently been directed towards the preparation of lithium by the reduction of lithium compounds at high temperatures under reduced pressure, so that the lithium metal formed distils off and is recovered by condensation. This method of preparation, termed vacuum metallurgy, has been the subject of a number of patents.[15,16-16c] There is, however, no evidence that such processes have as yet found any industrial application. Experimental work appears to have been confined to the laboratory or the small semi-technical scale and is discussed elsewhere (see page 6).

THE MANUFACTURE OF LITHIUM BY ELECTROLYSIS

The Electrolysis of Solutions of Lithium Salts in Non-aqueous Solvents.

As yet no process for the manufacture of lithium by electrolysis of solutions of lithium salts in non-aqueous solvents appears to have been operated commercially. However, a potential industrial route to the metal is outlined in a patent which describes the production of 10lb. of lithium per hr. by a cyclic process in a cell having an iron cathode, a carbon anode and operating at 18,000amp. and 5V., with a current density of 20amp. per sq.dm. of electrode surface. The cell feed is a liquid consisting of liquid ammonia containing 2 mols. of lithium perchlorate per litre, and the feed rate is such that the cell is supplied with 154lb. of lithium perchlorate per hr. The cathode product is a bronze coloured solution containing 12·5% by weight of lithium metal and floats on the electrolyte and is removed from the cell. The ammonia is then evaporated from the solution and recompressed for subsequent return to the cell. The anode product contains ammonia, ammonium perchlorate and lithium perchlorate. The liquid ammonia is evaporated and returned to the compressor. Water and lithium carbonate equivalent to the ammonium perchlorate are then added to the residue and ammonium carbonate obtained as a by-product. Following evaporation of the solution and drying of the salt, substantially anhydrous lithium perchlorate is obtained. Approximately 40% by weight of the lithium perchlorate feed is recycled as a result of the presence of the salt in the anolyte as it is removed from the cell. The necessary make-up ammonia is added to the recovered liquid ammonia and the cell feed prepared by mixing the required amount of lithium perchlorate and ammonia to provide a cell feed of the stated concentration.

The cell continues to operate satisfactorily when small amounts of water are present in the lithium salt which is dissolved in the anhydrous ammonia to form the electrolyte, but it is preferable to use an anhydrous salt, and means of drying the salt are described.

It is claimed that the cathode product is substantially free from an electrolyzed salt, and that metal of high purity is obtained on evaporation of the excess solvent.[16d]

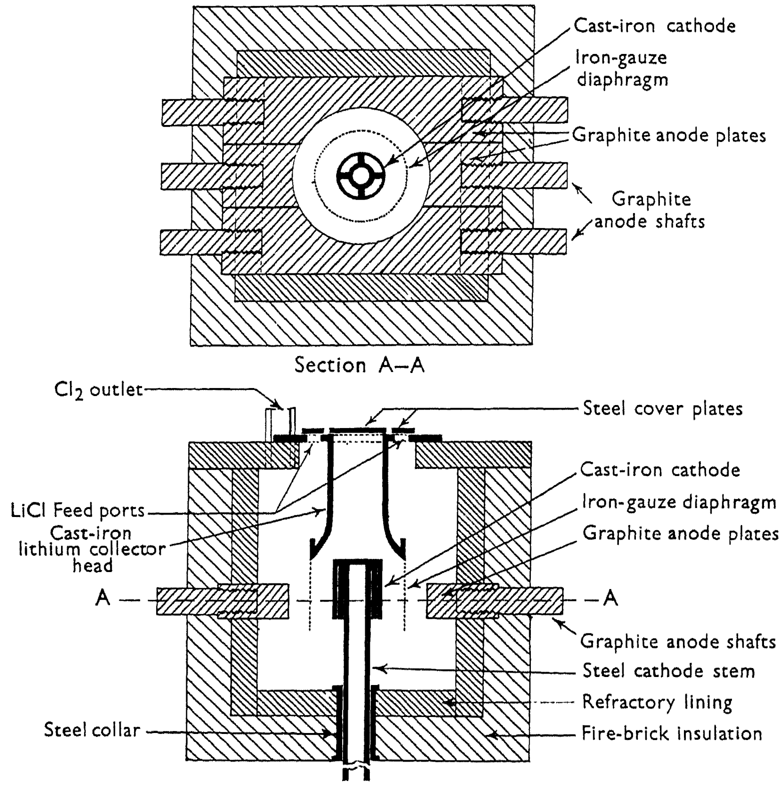
The Electrolysis of Fused Salts.

Electrolysis of a fused mixture of lithium chloride and potassium chloride appears to be the only process for the production of metallic lithium that has been operated successfully on the commercial scale.[17,18] Attempts to produce the metal continuously by the electrolysis of pure lithium chloride in the fused state have met with little success. With this electrolyte the cell voltage is found to increase rapidly with a corresponding fall in current, so that deposition of lithium soon ceases.[2] Moreover, as pure lithium chloride melts at 614°C., the operating temperature is comparatively high and both the fused chloride and the liberated lithium metal are extremely corrosive and rapidly attack the refractory lining of the cell.

The addition of potassium chloride to the bath removes these difficulties almost entirely, and the metal can be obtained in good yield by electrolyzing a fused bath consisting of equal weights of potassium and lithium chlorides.[17] The use of this mixed electrolyte has the further advantage that by selecting a melt of the required composition electrolysis can be carried out at temperatures around 400°–420°C., and at these lower temperatures the corrosive properties of the fused electrolyte and the molten lithium are greatly lessened.

The decomposition voltage of lithium chloride is lower than that of potassium chloride (*q.v.*), and it is found that the metal produced by the electrolysis of equal parts of fused potassium and lithium chlorides contains about 97% of lithium.[17]

A good deal of information has been published regarding the design and operation of a cell for the production of lithium at the Degussa plant at Rheinfelden, Germany.[17,18] The cell, shown diagrammatically in Figs. 1 and 2, consists of a square steel shell enclosing a firebrick box which serves to support and insulate the interior lining of the cell. This lining consists of a dense refractory. The cell is covered by a thick refractory plate having in the centre a large circular hole to accommodate the lithium metal collecting assembly. A smaller hole at one side of the cover plate serves for the removal of the chlorine gas produced during the electrolysis. The anode is an assembly of three horizontal graphite plates, with a circular opening in the centre of the assembly. Electrical connexion to the anode is made by six threaded graphite rods inserted externally. External electrical connexions to the source of electrical supply are conventional copper clamps and cable.


Cast-iron cathode
Iron-gauze diaphragm
Graphite anode plates
Graphite anode shafts
Section A–A
Cl_2 outlet
Steel cover plates
Cast-iron cathode
Iron-gauze diaphragm
Graphite anode plates
LiCl Feed ports
Cast-iron lithium collector head
A
A
Graphite anode shafts
Steel cathode stem
Refractory lining
Steel collar
Fire-brick insulation

FIGS. 1 and 2. DEGUSSA LITHIUM CELL

The cathode is a vertical steel shaft attached to a hollow cast steel head. The shaft passes out of the cell through a cast steel sleeve sealed into the bottom of the cell. This serves to locate the cathode in the centre of the anode assembly. The collecting head for the lithium metal is suspended from a circular plate which covers the large opening in the cell cover plate. This head is cylindrical and has a bell shaped bottom to facilitate the collection of the globules of molten lithium deposited on the cathode during the electrolysis: its lower edge has a rim which serves to support the diaphragm. This diaphragm, which is necessary to separate the chlorine liberated at the anode from the lithium deposited at the cathode, is a cylindrical screen of 24 mesh iron wire gauze extending a little below the lower side of the anode plates. The horizontal plate carrying the collecting head has a central opening for removing the molten lithium.

During operation this opening is kept covered with a steel plate except when lithium is being removed. Two bean shaped openings alongside, also normally covered with plates, serve for adding the make up lithium chloride to the bath.

The electrolyte is a fused mixture of 52% of lithium chloride and 48% of potassium chloride. Purity of the electrolyte and the cell feed is most important, and it is desirable that the lithium chloride should be substantially anhydrous. The presence of sulphates, silica, barium, calcium, iron oxide or appreciable amounts of sodium are considered to be especially disturbing in the electrolysis, and reduce current efficiency and cell output.[19]

Recent work has shown that hydrolytic decomposition takes place during the fusion of a eutectic mixture of lithium chloride–potassium chloride containing traces of moisture if the fusion conditions are not controlled. The resultant contamination by hydroxyl ion reduces the efficiency of the mixture for electrolysis. A method of preparation involving drying under a moderate vacuum, fusion under anhydrous hydrogen chloride, and removal of hydrogen chloride from the melt, is described.[19a]

Before adding the molten electrolyte to a cell for beginning operations, the collector head and cathode are removed and the cell is heated internally. When the cell container is considered hot enough, the cathode is replaced and the cell filled with the molten electrolyte. The electrolyzing current is then turned on in the absence of the collecting head and diaphragm. After working for about two hours in this fashion, the impurities that rise to the surface of the bath are removed by skimming. The collecting head and diaphragm are then placed in position and collection of the lithium metal is started. The cell is operated continuously, lithium chloride being added at regular intervals to replace the salt electrolyzed. A small make up of potassium chloride is also necessary from time to time to maintain the composition of the cell bath at the correct concentration. The current provides the heat necessary to keep the electrolyte in the molten condition and no external heating is required. The fused electrolyte in the collecting head is covered with a layer of high-boiling petroleum oil which forms a protective coating over the lithium which accumulates in the head. From time to time the metal is removed by scooping it out with a fine wire mesh ladle, which retains the lithium but permits most of the oil to run through, though sufficient is retained to prevent ignition of the molten metal on exposure to air. The chlorine gas liberated during the electrolysis is removed under suction and absorbed in a lime suspension circulated in a packed stoneware tower.

The Degussa plant is described as consisting of six cells, each producing 8·8–11 lb. (4–5kg.) daily with a maximum output of 295 lb. (134kg.) per month. Operating details are given in Table I.

A typical analysis of the metal produced is lithium 97%, potassium 1·3%

TABLE I. - ELECTROLYTIC PRODUCTION OF LITHIUM (DEGUSSA CELL)

Temperature of electrolyte	400°–420° C.
Current load	850–900 amps.
Voltage across cell	8–9 volts
Anode current density	1·4 amp. per cm.^{2}
Cathode current density	2·1 amp. per cm.^{2}
Current efficiency	85–90%
Production per cell per day	4·5kg.
Production per ampere hour	0·22–0·24 g.
Lithium chloride usage per lb. lithium	7·3kg.
Electrolyte capacity of cell	100kg.

and sodium 1·4%. The presence of even small amounts of sodium is undesirable in lithium intended for alloying purposes, and excessive amounts of sodium make the metal more easily combustible. In the early stages of the development of the manufacture of lithium, nitrogen as an impurity gave considerable trouble, the percentage present in the metal often being as high as 1%. Improved equipment and perfected methods of operation have now reduced the nitrogen content of the metal to about 0·03%.[2]

Electrolytic lithium is also manufactured in the United States, and the following description relates to a cell operated by the Lithium Corporation of America, and using as electrolyte a eutectic mixture of lithium and potassium chlorides.[20,20a] The cell is a steel box 4ft. × 6ft. in area and 3ft. deep, constructed of 1 inch boiler plate and lined with carbon blocks sealed with a carbonaceous cement. The cell body is supported in a brick lined shell and heated by gas to maintain the electrolyte in the molten condition. Four graphite anodes each 8in. in diameter and 6ft. long are supported from above and extend downward into the electrolyte. The cathodes are of steel. The cell is maintained under slight suction to remove the chlorine formed during electrolysis. In operation, the lithium metal accumulates at the cathode as drops about the size of marbles, and these quickly rise to the surface of the electrolyte and coalesce to form a pool of molten metal. It is found that a thin film of molten electrolyte forms on the surface of the lithium and protects it against atmospheric attack.

The accumulated lithium in ladled out of the cell from time to time. The metal is then allowed to cool in the ladle to a temperature below the melting point of the electrolyte but above the melting point of lithium. Thus, any electrolyte inadvertently picked up in the skimming operation solidifies in the ladle and the molten lithium, substantially free from electrolyte contamination, is then cast in ingot moulds.

The lithium is further purified by remelting at a temperature somewhat above its melting point. It is claimed that the insolubles in the metal either float to the surface, where they are skimmed off, or sink to the bottom of the pot. The molten lithium can then be tapped off through a spout set in the side of the melting furnace. During the melting a blanket of oil vapour serves to protect the surface of the molten metal from oxidation or nitriding. The cell life is about three months, after which the cell is shut down for relining. Normally the anodes last for a similar period. The cell operates at 8600amp. and 6–6·5V., with an output of 90lb. of lithium metal per day. A typical analysis of the product is as follows: sodium 0·06, potassium 0·01, calcium 0·02, nitrogen 0·06, iron 0·001%.

The electrolysis of lithium chloride-potassium chloride melts containing lithium carbonate has been investigated by Degussa, who found that when a mixture of 48% of lithium chloride, 48% of potassium chloride and 4% of lithium carbonate was electrolyzed, preferential decomposition of the carbonate took place. Trouble was experienced during electrolysis owing to foaming of the melt and mechanical destruction of the graphite electrodes.[20b]

Little further information has been published on the technical production of lithium. The electrolysis of a fused mixture of equal parts of potassium chloride and lithium chloride has been carried out in an iron cell lined with magnesium silicate, using a graphite anode and an iron cathode. The output of the cell averages 1 kg. of lithium per day at 225amp. and 17V. The current efficiency is about 85% and analysis of the product shows that it contains 0·23% of potassium, 0·5% of sodium and 0·19% of magnesium.[21] It is stated that the magnesium comes from the cell lining and that the sodium was initially present as an impurity in the potassium chloride used in the electrolytic mixture. Another cell is described as electrolyzing a fused mixture consisting of 6 molecular parts of lithium chloride and 4 molecular parts of potassium chloride at 410°C. using graphite anodes and a hollow conical cathode.[22] The lithium produced by this cell is said to contain not more than 2% of potassium.

The electrical conductance for fused lithium chloride and lithium chloride-potassium chloride melts has been studied by a number of workers[22a-22e,22g] and the enthalpy and heat capacity of the lithium chloride-potassium chloride eutectic has been determined over the temperature range 100°-840°C.[22f]

Lithium Alloys by Electrolysis.

Osborg has developed processes for producing lithium alloys electrolytically.[23-25] Alloys of lithium and the alkaline earth metals are produced by the electrolysis of a fused mixture of lithium, potassium and alkaline earth metal chlorides in the requisite proportions. Thus, for example, a cell is operated on the commercial scale in which the initial charge of 112lb. of fused bath contains 15·5% of potassium chloride, 14·5% of calcium chloride and 70% of lithium chloride. The cell operates at 1900amp. and 9·8V., with an anode and cathode density of 0·65 and 3·75amp. per cm.^{2} respectively, and produces an alloy containing approximately 50% of lithium and 50% of calcium. An hourly make up of 885g. of calcium chloride and 1800g. of lithium chloride is added during the electrolysis.

The preparation of lithium-lead alloys by electrolysis of a eutectic mixture of lithium chloride and potassium chloride in the presence of a molten lead cathode has been investigated. Alloys containing up to 5·9% lithium were prepared. The best results were obtained at a current density of 0·2-0·9 amp./sq.cm. at 360°-500°C. At higher temperatures the yield was reduced. The current efficiencies fell from approximately 100% at 0·1amp./sq.cm. to 50% at 3amp./sq.cm.[25a]

The design of a proposed cell for the manufacture of lithium-lead alloy by electrolysis of fused lithium chloride in the presence of a molten lead cathode has been described.[25b]

Recent work shows that magnesium-lithium alloys can be made in the molten state by electrolytic deposition of lithium on a solid magnesium cathode from a molten 50% lithium chloride-50% potassium chloride, or 75% lithium chloride-25% barium chloride electrolyte at temperatures ranging from 560°C. to 630°C. By careful selection of pure raw materials and materials of cell construction it is possible to avoid contamination of the alloy with sodium, which has a deleterious effect on alloy ductility.[25c]

It is also possible to produce an alloy directly on the cathode by using a solid cathode of a metal which can combine directly with the lithium alloy produced by the electrolysis.[25] Thus, by electrolyzing a bath containing calcium, sodium and lithium chlorides in the correct proportions, using a lead cathode, a lead alloy cathode containing 0·04% of lithium, 0·6% of sodium and 0·7% of calcium may be produced; this can then be melted and cast in a form suitable for use as a bearing metal. The electrolysis may be carried out using a molten lead cathode. Alloys of lithium with a heavy metal having a relatively high melting point, such as nickel, are prepared by electrolyzing fused baths containing lithium compounds using anodes of nickel and graphite in parallel. The lithium alloy is deposited at the cathode. By varying the amounts of current passing through the nickel and graphite anodes respectively, nickel alloys containing between 20 and 40% of lithium have been prepared. Lithium-magnesium alloys have been prepared by electrolyzing molten lithium chloride electrolytes using magnesium cathodes.[26] With a bath of lithium chloride (60%) and potassium chloride (40%) electrolyzed at 450°C., an alloy containing 35% of lithium is produced. By operating at 550° and 600°C. alloys containing 20 and 9% of lithium respectively may be obtained. Lithium-calcium alloys have been prepared by electrolyzing a fused lithium chloride-calcium chloride electrolyte containing 10–66% of lithium chloride at 600°C. The lithium content varied between 4·8 and 33·2%.[27] Lithium alloys of zinc, aluminium and copper-aluminium have also been produced by electrolysis.[27a]

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THE PURIFICATION, HANDLING AND STORAGE OF LITHIUM

The Purification of Lithium.

Unless highly purified raw materials are employed, lithium prepared in the laboratory may be expected to contain small amounts of impurities such as the other alkali metals. Crude commercial lithium contains appreciable quantities of sodium and potassium as well as other impurities. The chief impurity in sodium-free lithium is said to be nitrogen, with oxygen present to the extent of about 30 p.p.m.[1] These impurities may be undesirable if the metal is used for alloying purposes. Thus in magnesium–lithium alloys, the presence of metallic sodium is regarded as particularly deleterious.[2] Lithium of high purity now being produced on the commercial scale in the U.S.A.[3] by vacuum distillation of crude commercial lithium has a guaranteed maximum sodium content of 0·02% and normally contains 0·001% of sodium, 0·005% of potassium and 0·01% of calcium. Lithium is also being produced to the same specification with the chloride ion content limited to a maximum of 0·003%.

Little information is available on the purification of lithium by filtration of the molten metal. It has been suggested that filtration will remove the major portion of the insoluble materials from the molten metal, but the solubility–temperature diagrams for lithium oxide and lithium nitride in molten lithium do not appear to be known.[3] According to Trocki, lithium for use in a liquid metal heat transfer system may be purified by filtering the molten metal through a sintered stainless steel filter in order to remove oxide, but no figures are given for the oxygen content of the filtered product.[1]

A patent describes a method for the purification of lithium whereby impure lithium metal is placed in a metal container such as a steel tube with an opening at its lower end, and then immersed in a molten salt such as lithium chloride which does not react with lithium. The impurities in the lithium sink to the bottom of the tube and the purified metal rises to the top.[4] It is claimed that most of the volatile impurities can be removed from molten lithium by heating the metal *in vacuo* at temperatures around 400° C.[3]

Some attention has been given to distillation as a means of purifying lithium containing small amounts of sodium and potassium. Lithium containing potassium can be purified by distillation in hydrogen:[5] at 700°C. lithium hydride is formed and, being comparatively involatile under these conditions, can be freed from potassium which volatilizes. Subsequently, the pressure is reduced; the lithium hydride decomposes at 1000°C. and lithium distils over and may be condensed.

The purification of lithium may conveniently be effected by distilling the crude metal *in vacuo.*[6,11-11c] A small triple vacuum still for this operation has been described and its operation detailed.[6]

When lithium containing 0·5% of sodium is refined by distilling in argon under reduced pressure in a simple retort, the refined metal contains as little as 0·002% of sodium.[7,7a] At pressures up to 0·001 mm. the sodium content of the distillate varies little from this value, but when the pressure is increased to 0·74 mm. the sodium content of the product is quadrupled. There is little evidence of any formation of oxide, nitride or hydride when the pressures of oxygen, nitrogen or hydrogen are below 0·035 mm. The potassium content of the lithium metal distilled as above is reduced to a minimum of 0·006%.

An apparatus for the laboratory purification of small quantities of lithium by distillation has been described.[3] By operating at pressures of 10^{-5} to 5×10^{-5} mm. at temperatures of 450–500°C., lithium can be distilled at the rate of about 1 g. per hour. It is said that the pure distilled lithium so prepared does not darken on exposure to air as does the commercial metal, but retains its lustre for periods up to ten hours.

In another apparatus, with a 5 g. charge of lithium containing 2–3% of impurities, a yield of lithium (of purity at least 99·5%) equivalent to 60–70% of the initial charge is obtained in about 4 hours when distilling at a pressure of 5×10^{-5} mm. at a temperature around 500°C.[9] It is stated that when strontium is present as an impurity separation is poor because its vapour pressure curve is similar to that of lithium. The purity of the product is shown in Table II.

TABLE II.- PURIFICATION OF LITHIUM BY DISTILLATION

Constituent	Electrically Reduced Lithium		Thermally Reduced Lithium	
	Initial %	Final %	Initial %	Final %
Aluminium	>1	ND–<0·02	ND	ND–0·02
Barium	ND	ND–<0·02	0·03	<0·02
Calcium	0·05	<0·02	0·05	<0·02
Magnesium	<0·02	<0·02	0·3	<0·02–0·05
Sodium	0·5	<0·05	0·1	0·05
Silicon	0·1	<0·02	ND	ND
Strontium	ND	ND	>1	1–0·5

In the course of determinations of the heat capacity of lithium, two samples of the metal were purified by vacuum distillation in a stainless steel still at temperatures between 650 and 700°C. A chemical analysis of the first sample indicated a purity of 99·98 at.-%. In distilling the second sample the still itself was placed in a vacuum, and under these conditions lithium of 99·99 at.-% was obtained.[10]

Much of the work on the purification of lithium by distillation has been carried out in glassware, and some attention has been given to special glasses resistant to lithium.[12] Lithium reacts very strongly with glass, and glasses with lithium as the only alkali are no more resistant than ordinary soda glass. The best results are obtained by using a borate glass almost free from silica.[12] It is said that the sodium content of lithium-base alloys can be diminished by the use of a suitable flux or by bubbling nitrogen through the molten alloy.[2]

The theory of vacuum distillation of lithium has been discussed.[2a]

The Handling and Storage of Lithium.

Lithium is less reactive than the other alkali metals and can be handled at room temperatures as easily as calcium or barium. Although lithium reacts readily with water, neither the metal nor the evolved hydrogen burns spontaneously. The metal reacts slowly and preferentially with the nitrogen of the atmosphere, provided sufficient moisture is present to initiate the formation of lithium nitride.[13] The metal may be stored under oil or in an inert atmosphere.[13,14] Molten lithium is preferably prepared from dry castings.[3] The metal is generally shipped in the form of pigs which are submerged in mineral oil to avoid oxidation. If lithium has been stored under mineral oil this should be removed by washing with benzene or petroleum ether, as the metal tends to react when heated in the presence of mineral oil.[3] Lithium can however be melted and poured in an inert atmosphere such as paraffin vapour at temperatures up to 200°C.[13]

The storage of small amounts of lithium prepared in the laboratory has been described.[15] It is claimed that metal stored under mineral oil remains untarnished for periods exceeding two years. X-Ray specimens of pure lithium have been prepared by extruding the metal into vaseline to prevent oxidation, the lengths being then sealed in thin walled capillaries which were evacuated.[16]

A reactive form of lithium can be prepared by dissolving the massive metal in anhydrous liquid ammonia at low temperatures. Distillation of the ammonia from the solution leaves the lithium in a finely divided state distributed over the surface of the vessel. Nitrogen contamination amounts to less than 1%, provided sufficient time is allowed for the removal of the last traces of ammonia.[16a]

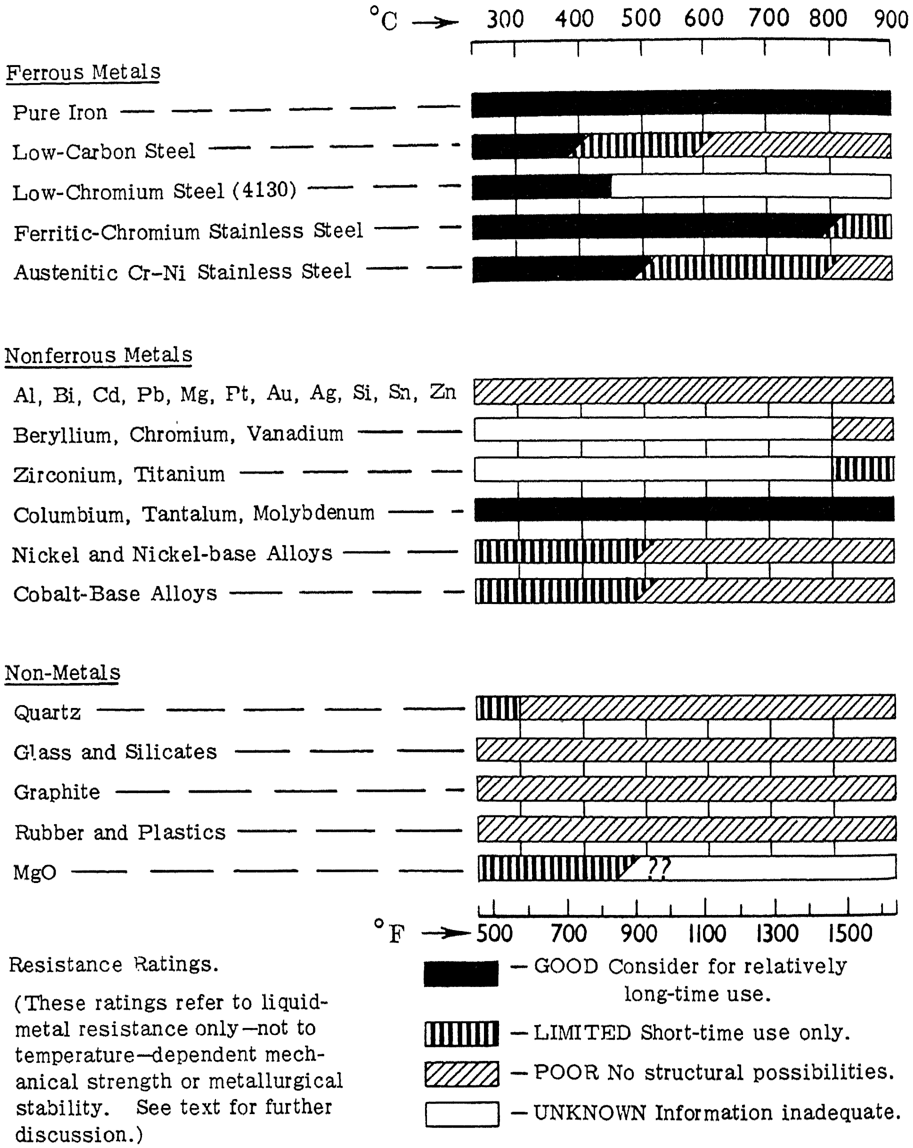
In general, molten lithium appears to be considerably more corrosive than the solid.[1,3,17,18,18a] Thus lithium severely attacks glass or the usual ceramics when melted in contact with them.[3,17] However, a technique is described for the preparation of samples of lithium in glass, whereby molten lithium is sucked into an evacuated glass capillary mould, and then frozen almost immediately before it has had time to react appreciably with the glass.[3a]

Thoroughly cleaned mild steel is recommended for handling the molten metal at temperatures up to 500°C. At higher temperatures, however, steel is rapidly attacked and decarburized by lithium.[17] It has been reported that both stainless steel and nickel are unsatisfactory for handling molten lithium but later information suggests that the trouble encountered was caused by the presence of lithium chloride or other electrolyte contamination in the lithium metal.[3] The resistance of materials to corrosion by lithium has been discussed by Miller.[17]

Armco iron has good resistance to attack by lithium at temperatures up to 600°C. and shows reasonable resistance at temperatures up to 1000°C. Nickel has good resistance to molten lithium at 225°C., limited resistance at 300°C. and poor resistance at temperatures over 600°C. Niobium, tantalum and molybdenum show relatively good resistance at 1000°C., but in the case of zirconium and titanium resistance is only fair. Aluminium, bismuth, cadmium, gold, lead, magnesium, platinum, silver, thallium, tin, zinc, manganese and silicon show poor resistance. Copper and copper alloys such as aluminium bronze, and high temperature cobalt base alloys are readily attacked by molten lithium.[17] The resistance of uranium to lithium at 600°C. has been studied.[17a]

Many of the reported corrosion tests have, however, used commercial lithium of questionable purity, and this may have given rise to misleading results. Among the contaminants frequently found dissolved or dispersed in or combined with molten lithium are nitrogen, oxygen, chlorine and hydrogen, and these may affect the corrosive nature of the metal. Thus lithium nitride, which is readily formed by the reaction of nitrogen with solid or liquid lithium, is extremely reactive, and no metal or ceramic material has been found which shows satisfactory resistance to it, although tests have been carried out using all the common metals, and also their oxides, nitrides and silicides.[17]

TABLE III.- RESISTANCE OF MATERIALS TO LIQUID LITHIUM[17]



(These ratings refer to liquid-metal resistance only—not to temperature—dependent mechanical strength or metallurgical stability. See text for further discussion.)

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Oxygen is often present in solid lithium as the hydroxide. Molten lithium hydroxide is extremely corrosive and no refractory metal has been found suitable for handling it. On being heated above its melting point, 455°C., the hydroxide tends to decompose to form the oxide.[17]

Lithium hydroxide or oxide can combine with or flux many refractories and in this way either remove protective films from metals or in some cases, increase the thickness of the films. Molten lithium chloride attacks iron and copper, and lithium hydride is reactive with metals and ceramics at high temperatures.[17]

Attempts to melt most samples of commercial lithium in quartz result in almost immediate failure of the container but sintered quartz has been recommended for use as a container for pure molten lithium up to 285°C.[19] Resistance is said to be poor when the lithium contains lithium oxide or nitride.[17] At temperatures above 285°C. lithium silicide is formed. Molten lithium penetrates magnesium but does not otherwise attack it, whereas molten lithium attacks most oxides of other structural metals and also carbides, silicides, rubber and plastics.[17] Molten lithium reacts with cement with explosive violence and at high temperatures rapid reaction occurs with common insulating materials such as asbestos and mica, and contrary to what is said previously, magnesia (1). Molten lithium also attacks dry sand at high temperatures.[19a] Near its melting point lithium does not attack Dow-Corning Silicone D.C. 550.[17]

A number of tests have been made to determine the effectiveness of various extinguishing agents on lithium fires.[1] The dry powders tested included Pyrene GI, zirconium silicate, potassium chloride, lithium chloride and graphite. Graphite powdered to pass through a 100 mesh screen gives satisfactory control of lithium fires. Potassium chloride may also be used and is cleaner to handle. These materials must be thoroughly dry. In no case should carbon dioxide, carbon tetrachloride or acid–soda fire extinguishers be used on lithium fires owing to the danger of the formation of explosive compounds. Residues must be handled with care. Thus lithium liberates sodium from salt and soda ash, and the residue from a lithium fire may be more reactive than the original lithium. The residue from a lithium fire extinguished with graphite may form acetylene in the presence of water.[19a]

The safety precautions to be observed by persons handling lithium have been discussed.[1,3,14,14a] In this connexion it should be noted that molten lithium may burn with an intense flame when it comes in contact with moist skin.[3] A protective device for the face and head has been described.[3] An investigation into the degree of protection afforded by various materials used for fire resisting clothing showed that the only material tested which afforded any substantial protection was chrome leather.[1]

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THE USES OF LITHIUM

In the original Treatise no uses are recorded for metallic lithium either in the laboratory or in industry. During the last twenty-five years, however, a large number of applications for the metal have developed in various fields of chemistry and metallurgy, though there is little information as to the actual amounts of metal assignable to the various uses. Some of the more important uses of lithium are discussed briefly below, but for more detailed information the reader should consult the original literature, and technological encyclopædias such as Thorpe[1] or Kirk Othmer.[2] An excellent comprehensive survey of uses for lithium was published by Osborg in 1935[3] and the subject has been reviewed more recently by other authors.[4-15l]

Metallic lithium is used in the preparation of lithium compounds such as lithium hydride.[16,17] In circumstances where the weight of the standard hydrogen gas cylinder is a drawback, this compound, which can be stored and transported in light canisters, can provide a convenient source of hydrogen by reaction with water. During the 1939–1945 war considerable quantities of lithium hydride were manufactured for use in inflating military balloons. Lithium hydride has also been used as a submarine fuel by burning it with oxygen.[18]

The reactivity of lithium in organic syntheses has been contrasted with that of the other alkali metals, and comparative figures have been given for yields obtained with lithium and sodium in a number of organic reactions.[18a] Lithium can replace magnesium in the Grignard reaction, and lithium alkyls and aryls are readily obtained in this way.[3,19,20] Two important features characteristic of the lithium Grignard reaction are its vigour, and its diversity, which offer possibilities beyond the scope of the conventional magnesium Grignard reactions.

Lithium is used as a catalyst in making synthetic rubber.[20a]

The preparation of metallic powders by reducing a metal compound with the lithium addition product of the ethers of polyhydric alcohols such as glycol ether, has been patented.[21] The process has been proposed for the preparation of powdered iron, nickel, cobalt, manganese, molybdenum, zinc, tin or silver. Alloy powders or powder mixtures of these metals can also be obtained.

The production of uranium by the reduction of uranium compounds with lithium or lithium sodium or potassium alloys, has been patented.[21a]

The feasibility of titanium production by the reduction of titanium tetrachloride with lithium has been discussed.[21b]

Lithium is effective in removing nitrogen from inert gases such as helium.[22] The metal may also be used as a 'getter' or scavenger material for removing the last traces of gases from various types of vacuum tubes.[23]

It has recently been suggested that metallic lithium is used in the manufacture of tritium for use in the hydrogen bomb. Lithium-6, an abundant isotope present in natural lithium, yields tritium when bombarded with neutrons.[24]

The application of molten lithium as a rocket propellant fuel has been discussed. It would appear that lithium must be ranked as one of the best-performing fuel elements.[25]

Molten lithium offers interesting characteristics as a heat transfer fluid in high temperature systems.[26-26c] Thus lithium is the lighest metal, and has a moderately low melting point, a high boiling point, a high specific heat and a comparatively high conductivity. Its low density permits the use of high fluid velocities without encountering high pressure drop. Experience with such systems has however been limited to a few units of relatively small capacity. The design, construction and operation of a heat transfer system employing molten lithium has been described in detail.[26] The system was designed to operate with maximum and minimum temperatures of approximately 1450° F. and 677° F. respectively, and was used to determine heat transfer coefficients in a lithium-to-lithium heat exchanger at a total heat flux of 1,000,000 B.T.U. per sq. ft. per hour.

Lithium has many attractive properties as a heat transfer medium. However it has one nuclear property to which there is a major objection, and that is the high absorption cross section of the ^{6}Li isotope for thermal neutrons. This leads to inefficient utilization of neutrons produced in the fission process. Fortunately the ^{7}Li isotope, which has a natural abundance of 92·57%, has a very low absorption cross section, and may be prepared from natural lithium by isotopic separation.[26b]

The principal industrial applications for lithium lie however in the field of metallurgy. Thus the metal is used extensively as a scavenger for refining molten metals such as iron, nickel, copper, zinc and their alloys.[3,27,36,36a] The lithium may conveniently be introduced into the molten heavy metal as an alloy such as lithium calcium, which is the preferred form though master alloys consisting of lithium and the metal to be treated are also effective. These lithium alloys react readily with deleterious impurities in the molten heavy metal, such as oxygen, hydrogen, nitrogen, carbon, oxides, sulphides, sulphur dioxide or silicates. Treatment is most effective when applied immediately before pouring, and in most cases satisfactory results can be obtained by the addition of as little as 0·01–0·03% of lithium.[3] Lithium is used in the degasification of copper and has a marked effect on the conductivity of cast copper and copper wire. Thus for example as little as 0·005 to 0·01% of lithium in copper wire increases the conductivity by 20%.[31] Copper deoxidized with lithium has also good mechanical properties.[28-34]

Lithium is also used for the degasification of nickel bronze and cast monel metal.[35]

In general it may be said that heavy metals degassed with lithium show a marked improvement in their physical and mechanical properties. Grey cast iron which has been treated with lithium can be poured more readily, and shows improved machinability and tensile strength and increased hardness, though the impact strength is somewhat reduced.[36] There are indications that the yield points of carbon steels are increased by lithium treatment,[3] and stainless steels are thus improved in yield point, tensile strength, hardness and corrosion resistance, whilst carbide precipitation on solidification is radically reduced.[3]

The presence of lithium in the copper electrodes used in the fixation of nitrogen by the arc process reduces the voltage and increases the yield of nitric oxide.[37]

A number of lithium alloys are of value in engineering. In general the presence of a fraction of 1% of lithium improves the characteristics of the base metal, imparts hardness and toughness, and increases the tensile strength.[38]

During the 1914-1918 war an aluminium-lithium alloy, 'Scleron', was developed in Germany by Metallgesellschaft.[38,39] A typical composition for a 'Scleron' alloy is:-

Aluminium	83%
Zinc	12%
Copper	2%
Manganese	0·5–1%
Iron	0·5%
Silicon	0·5%
Lithium	0·1%

The physical properties of the alloy are similar to those of mild steel or brass, and its tensile strength, elastic properties and hardness are reported to be superior to those of Duralumin.[3,38,39]

The presence of lithium in magnesium improves its physical and mechanical properties:[40] binary alloys containing 11% of lithium have surprisingly good corrosion resistance.[40,41]

Lithium-containing lead alloys for bearings have been made by Metallgesellschaft since 1926.[14] The alloys are called 'B metal' or 'Bahnmetall' because they have been used extensively for railway bearings, and they contain 0·04% of lithium together with small amounts of calcium, sodium, potassium and aluminium.[14] Lithium is the most effective constituent of B metal, imparting hardness at high temperatures with high resistance to deformation and satisfactory wearing properties.[42,43] In 1943 the output of Bahnmetall was 977,000 kg.[14] The casting and physical properties of lead are considerably improved by adding 0·005% or less of lithium. Lead-lithium alloys containing small amounts of bismuth have been used for the manufacture of cable sheaths.[44] The presence of lithium improves self-fluxing brazing alloys.[44a] The addition of 0·25% of lithium to silver-copper-zinc solders improves fluidity and wetting, and also the tensile and break strengths of the joints.[45]

The use of lithium in controlling furnace atmospheres for the heat treatment of metals such as steel has been the subject of a number of patents.[46-53] It is claimed that lithium reacts with oxygen, moisture and other oxidizing gases, and so completely nullifies their destructive action on the metal under treatment. It is, however, convenient to prepare the lithium *in situ* by the reduction of lithium compounds with suitable reducing agents.

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SECTION III

THE PHYSICAL PROPERTIES OF LITHIUM

By W.H. WILSON

Structure, Atomic and Ionic Radii, Etc.

Freshly cut surfaces of lithium are silvery-white, but they tarnish rapidly in air. When immersed in liquid nitrogen the metal remains silvery almost indefinitely;[1] specimens stored in liquid air also retain their bright metallic surfaces for a considerable time.[2] An excellent metallographic polish can be given to lithium by swabbing gently with cold methyl or ethyl alcohol.[3] The best results are obtained with methyl alcohol saturated with the reaction product, lithium methoxide. The slower reaction with higher alcohols leads to etch pitting rather than polish attack, and butyl and amyl alcohols have been used for macroetching.[3] Single-crystal specimens of lithium have been obtained by cooling the metal very slowly below its melting point.[4] Bender[5] was unable to obtain single crystal rods of lithium by methods which were successful with sodium and potassium.

At ordinary temperatures lithium crystallizes as a body-centred cube,[6-11] and the same structure exists down to the temperature of liquid air.[1,2,12] The unit cell contains two atoms and the Laue symmetry has been given as $m3m$.[11] Perlitz and Aruja[10] concluded that the space group was one of the following: T^3–$I23$, T_{α}^{3}–$I\bar{4}3m$, T_h^5–$Im3$, O^5–$I43$, O_h^9–$Im3m$. Several precise determinations of the unit cell dimensions at room temperature have been made recently: at 20°C. the values are 3·5023 ± 0·0002 kX. (equivalent to 3·5094 A.),[4] and 3·5016 ± 0·0002 kX. (equivalent to 3·5087 A.).[13] The small difference between these two determinations appears to be due to differences in the purity of the lithium samples. That used for the latter determination was virtually free from sodium and is claimed to be the purer material. Using 99·92% pure material, 3·5025 kX. (3·5096 A.) has been obtained at 18°C.[2] Older values of the lattice constant[6-10] – usually quoted to only three significant figures – vary between 3·50 and 3·51 A. and are in general agreement with those given above. The atomic radius is 1·52 A. Lattice parameters between room temperature and liquid air temperatures are given in Table I;[2] the variation (in kX. units) is closely represented by the equation: $a_t = a_0 (1 + \alpha t + \beta t^2 + \gamma t^3)$ where $a_0 = 3{\cdot}4992$ kX., $\alpha = 4{\cdot}6640 \times 10^{-5}$, $\beta = 3{\cdot}8791 \times 10^{-8}$, $\gamma = -11{\cdot}445 \times 10^{-11}$ and t is in °C.

TABLE I. - LATTICE PARAMETER OF LITHIUM

Temp. °C.	+20	–30	–60	–100	–140	–180	–183	–194
Lattice Parameter (kX.)	3·5025	3·4944	3·4899	3·4847	3·4802	3·4965	3·4763	3·4755
Lattice Parameter (A.)	3·5096	3·5015	3·4969	3·4917	3·4872	3·4835	3·4833	3·4825

Other values obtained in the region of liquid air temperature are 3·46 A. at –173°C.,[12] 3·4832 A. at –183°C.,[4] 3·4853 A. at –183°C.,[13] and 3·493 A. at

-195°C.[1]

At still lower temperatures lithium undergoes a spontaneous partial transformation to a close-packed hexagonal structure.[1,14] This transformation, which is accompanied by audible clicks, proceeds while the temperature is lowered below 72°K., but soon stops when the temperature is held constant or is raised slightly. The amount of the low temperature phase increases as the temperature is lowered and reaches approximately 50% at 63°K. Even at ~4°K. there remains a large amount of the body-centred cube structure which at this temperature has a lattice parameter of 3·472 ± 0·002 *kX*.[13] The reversion, which occurs on heating over a 30–50°C. range above 100°K., has similar characteristics, being halted by constant or lowering temperatures.[1] The exact value of the temperature required for complete reversion depends on the rate of heating and on the time during which the temperature is held above 100°K. With rapid heating the reversion is accompanied by audible clicks, but these are few or absent on slow heating. At -195°C. the unit cell dimension of the hexagonal close-packed structure is 3·086 A. and its axial ratio is 1·563.[14,15] Because of the similarity of this transformation to the change of austentite into martensite in steels, the close-packed hexagonal structure is sometimes referred to as 'lithium martensite.' The metallographic characteristics of lithium martensite have been studied.[3]

Although no spontaneous transformation occurs in lithium at liquid nitrogen temperature, a transformation from the normal body-centred cube to a face-centred cube can be induced at this temperature by cold working.[1,16] The face-centred phase forms with audible clicks during cold work at temperatures below 95°K., and its amount increases with increasing deformation below this critical value. Cold work stabilizes the body-centred form against further transformation on subsequent cooling and also against the reversion which can occur on heating to temperatures over 150°K. At -195°C. the lattice constant for the face-centred cube is 4·40 A., corresponding to an atomic radius of 1·55 A.[1] The density of this form is almost identical with that of the usual form. The expansion in atomic radius accompanying the transformation from a body-centred cube with a co-ordination number of 8 to a face-centred cube with a co-ordination number of 12 is 2·91%. Other measurements have given the lattice parameter of the body-centred and face-centred structures existing together at -194°C. as 3·4830 A. and 4·379 A. respectively.[2] When a specimen of lithium that has been compressed at liquid air temperatures and contains co-existing body-centred and face-centred structures is annealed at room temperature and then cooled to liquid air temperature, only the body-centred cube *X*-ray reflexions remain, but some of these are split into two.[2]

A suggestion that lithium crystallizes with a unit cell containing eight Li_2^+ molecules[17] is not supported by later work.[11]

Bidwell[18] observed breaks in the electrical resistance–temperature and thermoelectric power–temperature curves for lithium at a temperature of ~50°C. suggesting a phase transition (see pages 43–44). *X*-Ray diffraction experiments by the same worker indicated that the change is not from one crystalline pattern to another, but that a gradual fading-out or obliteration of the lattice structure occurs above this temperature.[19]

The atomic radial distribution curve for liquid lithium at 200°C. has been investigated by *X*-ray diffraction experiments.[20,21] At this temperature liquid lithium has 9·8 nearest neighbours at 3·24 A. compared with 8 atoms at 3·03 A. and 6 atoms at 3·50 A. in the solid.

Lithium, having the simplest electronic structure of the metallic elements, has been the subject of considerable theoretical study. It provides the closest approach to the 'ideal metal' of the electron theories since the electron cloud of the ion is small compared with the distance between atoms in the crystal. Wave-mechanical treatments of the constitution, energy and bonding of lithium have been given by numerous authors.[22-30m] A value of 3·02 A. has been estimated[31] for the lithium-lithium one-electron bond distance, and the electron distribution function for the free lithium atom[24,32] suggests a similar value of 3·2 A. Pauling[33,34] has thus pictured the lithium crystal involving both one-electron bonds and electron pair bonds, with resonance of these bonds among the various pairs of atoms. Theoretical values for many physical properties of lithium have been obtained by the application of quantum mechanical methods: in general, they are in fair agreement with experiment.

Both valence-bond and molecular orbital methods have been used in wave-mechanical treatments of the Li_2 molecule.[35-41] The Li_2^+ ion molecule has also been treated.[31,42]

Various attempts have been made to establish sets of ionic radii from which interionic distances can be obtained by summation.[33,43] Earlier attempts have been reviewed by Pauling[33] who, in formulating a semi-empirical set of such radii, selected a value of 0·60 A. for Li^+. This value was so chosen that, combined with an oxygen radius of 1·40 A., it was in agreement with the observed Li^+O^{--} distance of 2·00 A. in Li_2O. A previous treatment by Goldschmidt[44] gave 0·78 A. for the radius of the lithium ion.

Density and Thermal Expansion

The density of lithium at 18°C. has been reported as 0·5862[45] and at 20°C. as 0·546,[46] but it is probable that the density of the pure metal is more accurately represented by the much older value of 0·534 at 20°C.[47] which agrees well with X-ray diffraction data.[8,10] From the most recent and precise determinations of the lattice constant,[2,4,13] a value of 0·533 may be calculated for the density at 20°C. At −173°C. the density calculated from X-ray data is 0·553, and the same value has been given for absolute zero.[12] The atomic volume at absolute zero is 12·56 c.c.[12] Recent low temperature measurements[256] have given the density at 77°K. as 0·56 and at 4·2°K. as $0{\cdot}56_4$.

A direct determination of the density of liquid lithium at 195°C. gave 0·46 ± 0·01.[20] Values at higher temperatures are:-[48,49]

T, °C.	200	400	600	800	1000
d	0·507	0·490	0·474	0·457	0·441

Values of the coefficient of linear thermal expansion obtained from macroscopic measurements at temperatures below 0°C. are shown in Table II.[50]

TABLE II. - COEFFICIENT OF THERMAL EXPANSION OF LITHIUM

T, °K.	95	115	135	155	175	195	215	235	255	270
$\alpha \times 10^6$	17·0	23·0	28·5	32·7	36·3	39·1	41·4	43·2	44·7	45·7

Calculated values of the coefficient[50,51] are in good agreement with experiment, and there is approximate agreement with X-ray measurements.[13] A recent X-ray study[2] has given values of the mean thermal coefficient of expansion $[\alpha_{mean} = (a_t - a_0)/a_0 t]$ ranging from $3{\cdot}5 \times 10^{-5}$ at −194°C. to $4{\cdot}7 \times 10^{-5}$ at 20°C. ($4{\cdot}57 \times 10^{-5}$ at −30°C.; $4{\cdot}33 \times 10^{-5}$ at −70°C.; $4{\cdot}09 \times 10^{-5}$ at −110°C.; and $3{\cdot}81 \times 10^{-5}$ at −150°C.). From the expression for a_t (see page 31), the temperature variation of the mean coefficient of expansion is given by:-

$$\alpha_{mean} = 4{\cdot}6640 \times 10^{-5} + 3{\cdot}879 \times 10^{-8} t - 11{\cdot}445 \times 10^{-11} t^2 \ (t \text{ in } {}^\circ\text{C.}).$$

Bridgman[52,53] has measured the effect of pressure on the mean linear thermal expansion over the range 0–95°C. (see Table III, page 34).

TABLE III.- EFFECT OF PRESSURE ON THE THERMAL EXPANSION OF LITHIUM

Pressure, kg./cm.^{2}	0	2,000	4,000	6,000	8,000	10,000	12,000	14,000	16,000	18,000	20,000
$\alpha_{(0\text{ to }95^\circ\text{C.})} \times 10^5$	$5{\cdot}6$	$5{\cdot}1_5$	$4{\cdot}7_3$	$4{\cdot}3_4$	$4{\cdot}0_0$	$3{\cdot}7_0$	$3{\cdot}4_5$	$3{\cdot}2_5$	$3{\cdot}0_6$	$2{\cdot}8_8$	$2{\cdot}7_3$

Mechanical and Elastic Properties

The extensive investigations of Bridgman have yielded data on the compressibility of lithium to progressively higher pressures as new apparatus and techniques have been developed.[46,52-59] Table IV, based on his more recent results,[56,57] gives the change in the volume at room temperature over the pressure range 0–100,000kg./cm.^{2}.

TABLE IV.- EFFECT OF PRESSURE ON THE VOLUME OF LITHIUM AT ROOM TEMPERATURE

Pressure, kg./cm.^{2}	Relative Volume	Pressure, kg./cm.^{2}	Relative Volume
0	1·000	40,000	0·801
2,500	0·980	50,000	0·773
5,000	0·961	60,000	0·748
10,000	0·928	70,000	0·727
15,000	0·899	80,000	0·707
20,000	0·874	90,000	0·689
25,000	0·851	100,000	0·672
30,000	0·833		

The compressibilities of the five alkali metals are compared in the corresponding sub-section devoted to the physical properties of caesium. Equations have been given for the change in volume at 30° and 75°C. under pressures up to 12,000kg./cm.^{2},[46] but these require some revision in the light of later findings.[52,60] A recent study of the compression of the alkali metals at low temperatures[256] has given the figures in Table V for the relative volume of lithium at 4·2°K.

TABLE V.- EFFECT OF PRESSURE ON THE VOLUME OF LITHIUM AT 4·2°K.

Pressure, atm.	Relative Volume	Pressure, atm.	Relative Volume
0	1·0	3,000	0·979
500	0·996	4,000	0·972
1,000	$0{\cdot}992_5$	6,000	0·960
1,500	0·989	8,000	0·949
2,000	0·986	10,000	0·939

Several authors have given mathematical treatments of the compressibility of lithium.[28,61-64]

Bridgman has also studied the shearing stress for plastic flow as a function of hydrostatic pressure.[65] The shearing strength increases with temperature, and there is a break in the shearing strength–pressure curve at a pressure of about 12,000 kg./cm.^{2} It has been suggested that this break corresponds to a change in lattice brought about by shearing stress as distinct from the more common lattice changes produced by hydrostatic pressure.[65] At a pressure of 10,000 kg./cm.^{2} the shearing stress for plastic flow is about 100 kg./cm.^{2}; at 22,000 kg./cm.^{2} it is 850 kg./cm.^{2}; and at 50,000 kg./cm.^{2} it is 3,050 kg./cm.^{2}

Young's modulus has a value[66] of $4{\cdot}9 \times 10^{10}$ c.g.s. or $5{\cdot}0 \times 10^4$ kg./cm.^{2} Using this figure together with compressibility data of Richards,[67] Poisson's ratio has been calculated to be 0·42.[66] Elasticity measurements have been made on lithium polycrystals with varying degrees of anisotropy, and, by extrapolation, the elastic constants of quasi-isotropic polycrystals have been obtained.[5] A study of the diffuse reflexion of *X*-rays from single lithium crystals has indicated that the relative values of the elastic constants of lithium are similar to those of sodium.[68] Quantum mechanical calculations have given the following values (in dynes/cm.^{2}) for the elastic constants of lithium at absolute zero:-[69,70]

$$C_{11} = 1{\cdot}53 \times 10^{11};\quad C_{12} = 1{\cdot}19 \times 10^{11};\quad C_{44} = 1{\cdot}329 \times 10^{11}$$

The shear constant, C_{44}, has been related to the melting point and the interatomic distance.[71]

No recent work appears to have been done on the hardness of lithium.

Surface Tension and Viscosity

A recent determination[72] has given 398 dynes cm.$^{-1}$ for the surface tension of lithium at its melting point, the temperature coefficient being −0·14 dynes cm.$^{-1}$ degree^{-1} between the melting point and 480°C. Previously no experimental data were available, but estimates of 430[73] and 473[74] dynes cm.$^{-1}$ had been made for the surface tension at the melting point on the basis of other physical properties of lithium; the former figure was given as the most probable after estimating surface tensions by five different methods. Wave-mechanical treatments using the free-electron model have led to values of 400,[75] 639[76] and 890[77] dynes cm.$^{-1}$ for the surface tension at the melting point.

From surface tension data for fused salts and for salts in solution, the atomic parachor of lithium has been calculated as 50[78] and 46·8[79] respectively.

Using an oscillating-sphere method, with a nickel-lined sphere, the following values have been obtained for the viscosity of lithium:-[80]

Temp., °C.	183·4	193·2	208·1	216·0	250·8	285·5
η (millipoise)	5·918	5·749	5·541	5·406	4·917	4·548

These results have been expressed by the simple equation:-

$$\eta = 13{\cdot}86 \times 10^{-4}\, e^{664/T} \quad (T \text{ in } ^\circ\text{K.})$$

and by the more elaborate equation:-

$$\eta v^{1/3} = 1{\cdot}999 \times 10^{-3}\, e^{1171/vT} \quad (\text{where } v \text{ is the specific volume})$$

which makes allowance for the change of volume with temperature and gives a slightly closer fit. The viscosity at the melting point is 6·02 millipoise.[80] Novikov *et al*[80a] made measurements of the kinematic viscosity ($\nu = \mu/\text{density}$) of lithium between the melting point and 770°C., there being close agreement with the results of the above workers over the limited common temperature range. Interpolated values of kinematic viscosity (ν) and viscosities derived from them using the density data already given (see page 35)are:-

Temp. °C.	200	300	400	500	600	700
ν (millistokes)	11·2	9·3	8·2	7·4	6·7	6·2
η (millipoise)	5·7	4·6	4·0	3·6	3·2	2·9

Other viscosity values extending to still higher temperatures are:-[81]

Temp. °C.	205	260	371	538	983
η (millipoise)	6·0	5·4	4·8	4·5	4·1

Melting Point and Heat of Fusion

Recent values for the melting point of lithium: 178°C.,[82] 179 ± 1°C.,[83] 179·4°C.,[84] 179·5°C.,[85] 180·2 ± 0·1°C.[45] and 183°C.,[18] are in general agreement with the best representative value of 180°C. given previously (Mellor, II, 458). The triple point of pure lithium is 180·54°C.[86,87] The widely quoted value of 186°C. for the melting point of lithium appears to be considerably too high. Melting point-pressure curves for the alkali metals are compared in the corresponding sub-section devoted to the physical properties of caesium. The lithium curve is from previously quoted determinations of Bridgman (Mellor, II, 456).

The increase in volume on fusion is 1·57% or 0·0265 c.c. per gram.[45]

Calorimetric determinations of the heat of fusion have given 690 ± 30 g.-cal./g.atom,[85] 690 ± 70 g.-cal./g.atom,[83] and 717 ± 15 g.-cal./g.atom.[86,87] An earlier paper in which heat of fusion is related to the parachor quotes 3 kilojoules/g.atom (≡ 715 g.-cal./g.atom) as an experimental value for the heat of fusion of lithium.[88] From the lowering of its freezing point on addition of sodium, the heat of fusion of lithium has been calculated as 1320 g.-cal./g. atom.[84] From freezing point data for the binary systems Li–Mg,[89,90] Li–Tl[91] and Li–Zn,[92,93] Kelley[94] calculated values of 1190, 1070 and 1080 g.-cal./g. atom, respectively, for the heat of fusion of lithium and gave a weighted mean of 1100 g.-cal./g.atom; he points out, however, that this method is not very accurate and the direct determinations are to be preferred. Taking the heat of fusion as 690 g.-cal./g.atom, the entropy of fusion is 1·52 g.-cal./deg./g. atom.[85]

Vapour Pressure and Degree of Association

Hartmann and Schneider[95] determined the vapour pressure of lithium by measuring the temperature of boiling in an argon atmosphere at pressures of 17 to 94 mm. Hg:-

t °C.	935	947	968	988	1011	1035	1079	1080
p mm. Hg	17	22	28	35	46	57	92	94

Other workers have used effusion methods to obtain vapour pressures at lower temperatures. Bogros[96-98] has given a number of values between 459 and 572°C.:-

t °C.	459	470	490	510	537	563	572
p mm. Hg	0·0010	0·0017	0·0023	0·0031	0·0080	0·011	0·017

These can be expressed within 13% by the equation:-

$$\log_{10}p(\text{mm.}) = -6110/T + 5{\cdot}39 \qquad (T \text{ in } {}^{\circ}\text{K.}).$$

In studying the degree of association of alkali vapours, Lewis[99] obtained values for the vapour pressure of lithium in the region of 600°C. and gave the equation: $\log_{10}p(\text{mm.}) = -8090/T + 8{\cdot}505$ (T in °K.). This equation gives higher vapour pressures than have been found by other workers; the higher values have been ascribed[100,101] to the presence of sodium in the metal used. Using lithium from the same source but after heating it at 650°C. for a prolonged period to remove sodium, the following results have been obtained:-[100,101]

t °C.	462	476	497	515	538	550
p mm. Hg	0·0008	0·0013	0·0036	0·0044	0·0075	0·0134
t °C.	563	576	595	610	642	
p mm. Hg	0·0170	0·0232	0·0483	0·0599	0·1564	

These can be expressed by the equation:-

$$\log_{10}p(\text{mm.}) = -8172/T + 8{\cdot}012 \ (T \text{ in } {}^\circ\text{K.}).$$

In a review of vapour pressure data (1941) the equation:-

$$\log_{10}p(\text{mm.}) = -8143/T + 8{\cdot}0 \ (T \text{ in } {}^\circ\text{K.})$$

has been given as representing the vapour pressure of lithium within ± 10% between 1100 and 1400°K. and within ± 30% between 700 and 1600°K.[102]

The equilibrium constant for the dissociation of lithium molecules into atoms has been computed from spectroscopic data; the following values are for partial pressures in atmospheres:-[103]

T°K.	298·1	500	1000	1600	2000
$\log K = \log (P_{\text{Li}})^2/P_{\text{Li}_2}$	−15·540	−7·539	−1·570	+0·697	+1·456

By applying these results to the vapour pressure observations of Hartmann and Schneider,[95] the pressure of the lithium atoms has been represented by the equation:-

$$\log_{10}p_{\text{Li}}(\text{mm.}) = 11{\cdot}889 - 38{,}900/4{\cdot}575T - 1{\cdot}174 \log T.$$

At the predicted boiling point of 1599°K., the partial pressures of lithium atoms and molecules in the saturated vapour are 648 mm. and 112 mm. respectively. The experimental values of the equilibrium constant obtained by Lewis[99] in the region of 900°K. using a magnetic deflexion method are considerably greater than those given above. Lewis's values given for partial pressures in mm. are:-

T, °K.	852	876·5	902	909	926·5
$\log K$.	0·967	1·209	1·352	1·478	1·516

The heat of dissociation of the lithium molecule as calculated from these equilibrium constant data is 24·0 kg.-cal.[99]

Boiling Point, Heat of Vaporization

By extrapolation of vapour pressure data obtained at lower temperatures, the boiling point of lithium has been given as 1609 ± 5°K.,[95] 1530°K.[100] and 1590°K.[102]

A value of 22·03 has been given for Trouton's constant.[95] Estimates of the critical temperature and the chemical constant based on vapour pressure data are 2490°K. and 3·08 respectively.[95]

The latent heat of vaporization of lithium has been calculated by several workers from their vapour pressure measurements at various temperatures. Reported values, with the temperature range of the vapour pressure measurements shown in brackets, are 35·4 kg.-cal./g.atom[94] (935–1080°C.); 37·0 kg.-cal./g.atom[99] (~580–650°C.); 28·0 kg.-cal./g.atom[98] (459–572°C.); and 36·6 kg.-cal./g.atom[100] (462–642°C.). Utilizing the vapour pressure data of Hartmann and Schneider,[95] Kelley[104] has represented the heat of vaporization by the equation:-

$$\Delta H \ (\text{g.-cal./g.atom}) = 36{,}410 - 2{\cdot}53T,$$

and the free energy of vaporization by:-

$$\Delta F^\circ \ (\text{g.-cal./g.atom}) = 36{,}410 + 5{\cdot}83 \ T \log T - 40{\cdot}88 \ T.$$

At the boiling point (1645°K.), ΔH = 32,248 g.-cal./g.atom and ΔS = 19·6 g.-cal./g.atom/°K.[104] Computation of the latent heat of vaporization of lithium from the absorption spectra of the lithium halides has given a mean value of 29·6 ± 0·6 kg.-cal./g.atom.[105,106]

The U. S. Bureau of Standards[107] selected value (1952) for the heat of sublimation of lithium to monatomic vapour is 36·49 kg.-cal./g.atom at 0°K. and 37·07 kg.-cal./g.atom at 298·16°K., while the free energy of sublimation is 29·19 kg.-cal./g.atom at 298·16°K. A later publication[107a] gives the heat of sublimation to monatomic vapour as 38·05 kg.-cal./g.atom at 0°K. and 38·439 kg.-cal./g.atom at 298·16°K., and the free energy of sublimation as 30·57 kg.-cal./g.atom at 298·16°K. Kelley[104] gave 36·439 kg.-cal./g.atom for the heat of sublimation at 298·1°K. Quantum mechanical calculations of the heat of sublimation or cohesive energy are in fair agreement with these figures.[28,30e,30i,108-110]

Specific Heat, Heat Content and Entropy

Specific Heat.

The specific heat of lithium between 15°K. and room temperature has been measured by Simon and Swain.[111] Some of their values are given in Table VI (see below). Recent measurements[111a] of the specific heat between 1·5°K. have given the following results:-

T, °K.	1·5	2·0	2·5	3·0	3·5
C_p, g.-cal./g.atom/°C.	0·00066	0·00091	0·00127	0·00150	0·00186
T, °K.	4·0	5·0	6·0	7·0	8·0
C_p, g.-cal./g.atom/°C.	0·00227	0·00335	0·00491	0·00684	0·0091
T, °K.	9·0	10·0	12·0	18·0	20·0
C_p, g.-cal./g.atom/°C.	0·0119	0·0152	0·0238	0·0722	0·0953

Several series of measurements were made on the lithium sample, and reproducible results were obtained between 2·4°K. and 13°K. and above 17°K.: there was some lack of reproducibility below 2·4°K. and between 13° and 17°K. The value for the atomic heat at 20°K. agrees very well with that of Simon and Swain.[111] A plot of C_p/T against T^2 for the above results leads to $(0{\cdot}418 \pm 0{\cdot}008)T \times 10^{-3}$ g.-cal./g.atom^{-1}deg.$^{-1}$ for the electronic specific heat.[111a]

From cooling curves obtained in studying the thermal conductivity of lithium, Bidwell[112] calculated specific heats from 140°C. down to liquid hydrogen temperatures. The values are in fair agreement with those in Table VI over most of the range, although at the lowest temperatures Bidwell's values are considerably higher. At temperatures above +75°C. the atomic

TABLE VI. - THE SPECIFIC HEAT OF LITHIUM AT LOW TEMPERATURES

T(°K.)	Atomic Heat (g.-cal./g.atom)		T(°K.)	Atomic Heat (g.-cal./g.atom)	
	C_p	C_v		C_p	C_v
15	0·045		140	4·08	4·01
20	0·095		160	4·43	4·34
25	0·169		180	4·68	4·57
30	0·273		200	4·92	4·78
40	0·573		220	5·15	4·94
50	0·996	0·995	240	5·28	5·09
60	1·43	1·42	260	5·44	5·22
80	2·32	2·31	280	5·56	5·31
100	3·05	3·02	300	5·66	5·39
120	3·64	3·59			

heat at constant volume exceeds the Dulong and Petit maximum of 5·95, and it has been suggested that the excess is latent heat of crystallization required for disintegration of the crystal lattice.[112] Other workers[113] have determined C_p over a 180° range immediately below the melting point; the value at the melting point was 7·1 g.-cal./g.atom. There is a rise in the specific heat immediately below the melting point which is characteristic of the alkali metals; it is, however, less marked with lithium than with sodium or potassium. In reviewing high temperature thermal data up to 1933, Kelley[114] gave the equation:-

$$C_p = 0{\cdot}68 + 18{\cdot}0 \times 10^{-3}T \qquad (C_p \text{ in g.-cal./g.atom, } T \text{ in } ^\circ\text{K.})$$

as applying between 273 and 459°K. with an estimated accuracy of ± 10%. In a more recent publication the same author gives:-[115]

$$C_p = 3{\cdot}15 + 8{\cdot}40 \times 10^{-3}T \text{ (accuracy} \pm 3\% \text{ between } 298^\circ \text{ and } 452^\circ\text{K.)}$$

for solid lithium, and:-

$$C_p = 8{\cdot}93 - 0{\cdot}36 \times 10^{5}T^{-2} \text{ (accuracy} \pm 1\% \text{ between } 298^\circ \text{ and } 2000^\circ\text{K.)}$$

for diatomic lithium vapour.

In recent years several American workers have measured the specific heat of lithium at high temperatures. The calorimetric results of Bates and Smith[116] (500–1000°C.), Redmond and Lones[117] (200–1100°C.) and Douglas *et al.*[86,87] (m.p. to 900°C.) are reasonably concordant, while values obtained by Cabbage[118] (m.p. to 1000°) are considerably lower than those of the other workers for temperatures above 500°C. and exceed them at lower temperatures. Values of the heat capacity between 200° and 500°C. computed by Yagee and Untermeyer[119] from measurements of the relative cooling rates of lithium and aluminium also diverge from those of the above workers, being lower at 200° and higher at 500°C. Douglas *et al.*[86,87] give the following equations for the heat capacity in absolute joules per gram, t being in °C.:-

$$\begin{aligned} C_p \text{ (solid)} &= 3{\cdot}510 + 9{\cdot}25 \times 10^{-4}t + 3{\cdot}312 \times 10^{-5}t^2 - 8{\cdot}88 \times 10^{-8}t^3 \\ &\qquad\qquad (25^\circ \text{ to } 180{\cdot}54^\circ\text{C.}) \\ C_p \text{ (liq.)} &= 4{\cdot}5306 - 8{\cdot}38 \times 10^{-4}t \ (180{\cdot}54^\circ \text{ to } 421{\cdot}8^\circ\text{C.}) \\ C_p \text{ (liq.)} &= 4{\cdot}2076 - 7{\cdot}23 \times 10^{-5}t \ (421{\cdot}8^\circ \text{ to } 895{\cdot}3^\circ\text{C.}). \end{aligned}$$

Values at rounded temperatures are shown in Table VII together with other thermodynamic functions.[86,87] Simon and Swain's value[111] at 25°C., the only temperature common to both, is about 4% lower than that from the above equation.

Measurements by these two sets of workers of the heat capacity of synthetic sapphire over the common temperature range 140–280°K. also differed by the same amount, and Douglas *et al.* have used this relationship to apply corrections to the values of Simon and Swain. These corrected values have been used in calculating the standard molal enthalpy and entropy at 25°C. (see below). Heat capacities calculated from spectroscopic data for monatomic and diatomic lithium vapour are shown in Table VIIa.[107a]

The specific heat of lithium does not obey the Debye formula. Instead, the Debye characteristic temperature, θ, increases from a value of 328 at 15°K. to 430 at 300°K.[111] This anomalous behaviour has been the subject of much theoretical study. Simon and Swain[111] suggested that the change of θ with temperature could be explained by thermally excited transitions to some higher quantum level. Subsequent direct measurements of the thermal oscillations in lithium have shown, however, that between -190°C. and room

TABLE VII.- THERMODYNAMIC FUNCTIONS OF LITHIUM BETWEEN 298° AND 1200°K.

T, °K.	$(H^\circ - H_0^\circ)/T$, g.-cal./g.atom/°K.	S°, g.-cal./g.atom/°K.	$-(F^\circ - H_0^\circ)/T$, g.-cal./g.atom/°K.	C_p°, g.-cal./g.atom
298·16	3·656	6·777	3·121	5·892
300	3·670	6·814	3·144	5·899
400	4·306	8·596	4·290	6·599
453·7(s)	4·604	9·455	4·851	7·020
453·7(l)	6·184	11·035	4·851	7·264
500	6·281	11·738	5·457	7·200
600	6·422	13·038	6·616	7·060
700	6·504	14·116	7·612	6·928
800	6·556	15·041	8·845	6·916
900	6·595	15·854	9·259	6·904
1000	6·626	16·581	9·955	6·892
1100	6·649	17·238	10·589	6·880
1200	6·668	17·836	11·168	6·868

temperature the energy supplied to lithium goes entirely to atomic vibration and not to a quantum jump.[120,121] Following the generalized work of Blackman,[122] showing that changes of θ with temperature could be accounted for by a theory of specific heats which takes into account the atomic structure, Fuchs[69] has shown that if dispersion is neglected – as is the case in the Debye theory – the anisotropy of the alkali metals gives rise to the type of divergence from the Debye formula observed with lithium. Specific heats in fair agreement with the experimental values of Simon and Swain[111] have been calculated by evaluating the four discrete frequencies of atomic vibration in terms of the elastic constants of the lithium crystal and representing the residual degrees of freedom not covered by these modes by a Debye function with a correspondingly reduced characteristic temperature.[123]

Characteristic temperature values for lithium have been given by a number of authors in treatments of specific heat and other data.[5,50,68,69,111,111a,121,122,123a-c] A recent detailed study of characteristic temperature data has used several methods for calculating θD, the Debye characteristic temperature, from thermodynamic data and θR from electrical resistance data.[124] θR exhibits a maximum in the region of 80° to 100°K. although no discontinuity or anomaly is apparent in the resistance-temperature curve itself: θD shows no such maximum. While theory predicts that θD should be less than θR, the reverse applies for lithium above 100°K. At room temperature θR and θD have values of about 330 and 400 respectively.[124] When, in a later paper,[125] an allowance was made for the effects of thermal expansion, the value of θR was increased by about 20.

Heat Content or Enthalpy.

Using data available up to 1948, Kelley[115] formulated the following equation to represent the heat content or enthalpy of solid lithium between 298 and 452°K. with an accuracy of ± 3%:-

$$H_T - H_{298\cdot16} = 3\cdot15T + 4\cdot20 \times 10^{-3}T^2 - 1313 \text{ (}H\text{ in g.-cal./g.mole, }T\text{ in °K.).}$$

From vibration frequency data[126] the same author represented the heat content of lithium vapour between 298 and 2000°K. with an accuracy of ± 1% by the equation:-

$$H_T - H_{299\cdot16} = 8\cdot93T + 0\cdot36 \times 10^5T^{-1} - 2783,$$

TABLE VIIa.- THERMODYNAMIC FUNCTIONS FOR MONATOMIC AND DIATOMIC LITHIUM VAPOUR

T, °K.	$-\left[\frac{F^\circ - H^\circ_0}{T}\right]^*_1$	$-\left[\frac{F^\circ - H^\circ_0}{T}\right]^*_2$	$\left[\frac{H^\circ - H^\circ_0}{T}\right]^*_1$	$\left[\frac{H^\circ - H^\circ_0}{T}\right]^*_2$	$S_1{}^\circ$ *	$S_2{}^\circ$*	$C_{p1}{}^\circ$*	$C_{p2}{}^\circ$*
100	22·7487	-	4·9680	-	27·7167	-	4·9680	-
250	27·3008	37·969	4·9680	7·600	32·2688	45·569	4·9680	8·444
298·16	28·1760	39·294	4·9680	7·753	33·1440	47·047	4·9680	8·620
400	29·6358	41·636	4·9680	8·002	34·6038	49·638	4·9680	8·825
500	30·7444	43·442	4·9680	8·179	35·7124	51·621	4·9680	8·941
600	31·6501	44·94	4·9680	8·31	36·6181	53·25	4·9680	9·02
800	33·0793	47·36	4·9680	8·50	38·0473	55·86	4·9680	9·13
1000	34·1879	49·28	4·9680	8·64	39·1559	57·92	4·9680	9·22
1200	35·0937	50·86	4·9680	8·74	40·0617	59·60	4·9680	9·30
1400	35·8595	52·22	4·9680	8·83	40·8275	61·05	4·9684	9·37
1500	36·2022	52·83	4·9681	8·86	41·1703	61·69	4·9688	9·41
1600	36·5229	-	4·9681	-	41·4910	-	4·9696	-
1800	37·1080	-	4·9685	-	42·0765	-	4·9737	-
2000	37·6315	-	4·9694	-	42·6009	-	4·9831	-
2500	38·7411	-	4·9776	-	43·7187	-	5·0514	-
3000	39·6505	-	5·0017	-	44·6522	-	5·2098	-
3500	40·4274	-	5·0475	-	45·4749	-	5·4535	-

Subscript $_1$ refers to monatomic lithium vapour
Subscript $_2$ refers to diatomic lithium vapour
* in g.-cal./mole/°K.

the heat content being in g.-cal./g.mole, and T in °K.[115] Calorimetric measurements over the range 500 to 1000°C. have led to the equation:-

$$H_t - H_0 \text{ (g.-cal. per gram)} = 121 \pm 39 + 0{\cdot}962\ (\pm\ 0{\cdot}05)T$$

as representing the heat content of liquid lithium with a confidence limit of 95%.[116] More recent measurements on lithium of 99·98–99·99 atomic per cent purity, using an ice calorimeter and a drop method over the range 50 to 900°C., have given the following equation in which the heat content is in absolute joules per gram and t is in degrees C.:-[86,87]

$$H_t \text{ (solid)} - H_0 \text{ (solid)} = 3{\cdot}5096t + 4{\cdot}625\ (10^{-4})t^2 + 1{\cdot}1041\ (10^{-5})t^3 - 2{\cdot}221\ (10^{-8})t^4 \text{ (25 to 180·54°C.)}$$

$$H_t \text{ (liquid)} - H_0 \text{ (solid)} = 318{\cdot}07 + 4{\cdot}53026t - 4{\cdot}191\ (10^{-4})t^2 \text{ (180·54 to 420°C.)}$$

$$H_t \text{ (liquid)} - H_0 \text{ (solid)} = 386{\cdot}21 + 4{\cdot}20755t - 3{\cdot}615\ (10^{-5})t^2 \text{ (420 to 900°C.)}$$

From the low-temperature heat capacity data of Simon and Swain,[111] adjusted as described above, the heat content of solid lithium at 298·16°K. relative to that at 0°K. is 1090 g.-cal./g.atom.[86,87] Values of the heat content function based on the above equations and this value for 298°K. are given in Table VII (see page 40). The best single equation representing the heat content of liquid lithium (in absolute joules per g. at T°K.) between 453·70° and 1173°K. is:-[86]

$$H_T \text{ (liquid)} - H_{273{\cdot}16} \text{ (solid)} = -275{\cdot}73 + 3{\cdot}52675T + 3{\cdot}94442\ (10^{-4})T^2 - 9{\cdot}5669\ (10^{-8})T^3 - 1{\cdot}24649/T.$$

Heat content functions, calculated from spectroscopic data, for monatomic and diatomic lithium vapour are shown in Table VIIa together with other thermodynamic properties.[107a] The same source[107a] gives the heats of formation of monatomic and diatomic lithium vapour at 0°K. as 38·05 and 50·34kg.-cal./g.mole respectively.

Entropy.

Extrapolation of the low-temperature heat capacity data of Simon and Swain[111] leads to 6·70 ± 0·06 g.-cal./g.atom/°K. for the entropy of solid lithium at 298·16°K. After adjusting the same heat capacity data, as described above, Douglas and co-workers obtained $S_{298\cdot16}$ = 6·78 g.-cal./g.atom/°K.[86,87] Entropies for solid and liquid lithium obtained from calorimetric measurements up to 1200°K. are also shown in Table VII.[86,87]

For monatomic lithium vapour, the Sackur equation – to which must be added $R\ln 2$ to account for the multiplicity in the lowest energy state – gives 33·15 ± 0·01 g.-cal./g.atom/°K. for the entropy at 298·16°K.[127] The molecular constants of diatomic lithium vapour lead to $S^{\circ}_{298\cdot16}$ = 46·98 ± 0·10 g.-cal./mole/°K. of which 1·17 is the vibrational contribution and 45·81 the translational and rotational contribution.[127] Table VIIa contains entropy values for monatomic and diatomic lithium vapour calculated by Hall *et al.*[107a] in a recent survey of the thermodynamic properties of lithium and other alkali metals.

Thermal Conductivity

A modified Forbes bar method has given the values for the thermal conductivity of solid lithium shown in Table VIII.[112]

TABLE VIII.- THERMAL CONDUCTIVITY OF SOLID LITHIUM

Temp., °C.	−250	−200	−150	−100	−50	0	+50	+100	+150
k, g.-cal.sec.$^{-1}$cm.$^{-1}$°C.$^{-1}$	1·00	0·218	0·200	0·185	0·170	0·155	0·153	0·166	0·170

From 0 to −200°C. the thermal conductivity increases linearly, but with further decrease of temperature it rises sharply. A minimum thermal conductivity occurs at +40°C.; this point corresponds to breaks in the electrical resistance-temperature and thermoelectric power-temperature curves (see Fig. I, page 44). Between 80° and 120°K., MacDonald *et al.*[127a] obtained a thermal conductivity of about ·1 watt cm.$^{-1}$°C.$^{-1}$ (equivalent to 0·24g.-cal.sec.$^{-1}$cm.$^{-1}$°C.$^{-1}$). At lower temperatures it rose to a maximum of 5 to 7 watt cm.$^{-1}$°C.$^{-1}$ at around 20°K. An earlier study of the thermal conductivity of lithium using an indirect method involving the measurement of the electrical resistance of a lithium wire and its temperature coefficient of resistance gave k_t/k_0 = 2·9 at −253°C.; 1·16 at −182°C.; 1·02 at 20°C.; and 1·02 at 101°C.[128] The absolute value at 0°C. was estimated to be 0·17 g.-cal.sec.$^{-1}$cm.$^{-1}$°C.$^{-1}$ [131]

Measurements of the thermal conductivity of lithium[119] relative to that of sodium when taken in conjunction with other measurements of the thermal conductivity of sodium[129] lead to a value of 0·09 g.-cal.sec.$^{-1}$cm.$^{-1}$°C.$^{-1}$ for the thermal conductivity of liquid lithium between 218° and 233°C.[49] Recent direct measurements,[130] having an estimated accuracy of ± 10%, have been made on 99·8% pure liquid lithium between 420° and 1002°F.: interpolated values together with an extrapolation to the melting point are given in Table IX.

On the basis of the Wiedemann-Franz-Lorentz law relating thermal and electrical conductivities, the thermal conductivity of liquid lithium at its melting point has been estimated as 0·085 to 0·11 g.-cal.sec.$^{-1}$cm.$^{-1}$°C.$^{-1}$ [131]

The thermal conductivity of lithium has been related to its specific heat

TABLE IX.- THERMAL CONDUCTIVITY OF LIQUID LITHIUM

Temp., °F.	354	400	500	600	700	800	900	1000
k, B.Th.U.hr.$^{-1}$ft.$^{-1}$°F.$^{-1}$	27	27	26	25	24	22	20	18

and the absolute temperature, and the lattice and atomic contributions to the thermal conductivity at 0°C. are given as 0·150 and 0·006 respectively.[132]

The heat-transfer properties of liquid lithium have recently been considered.[133]

Electrical Resistance

Bidwell[112] found the specific resistance of lithium at 0°C. to be 0·885 × 10^{-5}, and he combined this with his earlier measurements of relative resistance[18] to give the following values of electrical conductivity:-

t°C.	-250	-200	-150	-100	-50	0	20	50	100	150
Conductivity	1050	116	36·1	21·1	15·00	11·55	10·35	9·44	8·13	7·14

Other measurements of relative resistance have been made over the temperature ranges 20 to 373°K.,[128] 1·2 to 273°K.,[134] 1·8 to 273°K.[135,136] and 18 to 100°K.,[127a] MacDonald and Mendelssohn made continuous measurements in the temperature interval between 1·8 and 20°K. – normally a difficult range to cover experimentally.[135,136] Below about 4°K. the resistance was constant, and for the samples they employed the residual resistance had R/R_0°C. values of 3 to 5 × 10^{-3}. In Table X the values of resistance are corrected for the residual resistance. In dealing with the values of Meissner,[128] who only went down to 20°K., the residual resistance of Meissner and Voigt[134] is employed.

TABLE X.- RELATIVE ELECTRICAL RESISTANCE OF LITHIUM

Temp. °K.	R/R_0°C.		
	(Meissner)	(Meissner and Voigt)	(MacDonald and Mendelssohn)
374·35	1·443	–	–
329·57	1·247	–	–
292·8	1·086	–	–
273	1·0	1·0	1·0
90·9	0·1689	–	–
90	–	–	0·171
86·3	–	0·1464	–
80·1	0·1255	–	–
77·7	–	0·1169	–
20·4	0·0015	0·0013$_2$	0·0013$_3$
17·8	–	–	0·0007$_6$
16·05	–	–	0·0004$_5$
14·8	–	–	0·0002$_9$
13·55	–	–	0·0002$_1$
12·3	–	–	0·0001$_4$
11·4	–	–	0·00009
4·2	–	0·0001$_8$	–
1·2	–	0·0000$_5$	–

According to Meissner,[128] the slope of the resistance-temperature curve is nearly constant between 0 and 100°C. although it falls off below 0°C. Bidwell,[18] however, noted a slight break in the curve at about 50°C. as well as a considerable increase in resistance as the melting point is reached (Fig. I). Below 20°K., the resistance after subtracting the residual resistance is proportional to the temperature raised to the power 4·52.[135] Recent work has shown that lithium is not superconducting at temperatures down to 0·08°K.:[137,138] earlier work had shown that this was true down to 1·7°K.[139]

For most metals the electrical resistance decreases on application of pressure and increases under tension. Lithium shows an anomalous behaviour in that its resistivity increases under pressure.[140] This applies to both the solid and liquid states, the magnitude of the coefficient for the liquid being greater than for the solid:[141] the ratio of the resistance of solid and liquid lithium is little affected by pressure.[141] Bridgman[140] has extended his earlier measurements (Mellor,II,460) to higher pressures and has obtained the values for the effect of pressure on electrical resistance shown in Table XI.

TABLE XI. - EFFECT OF PRESSURE ON THE ELECTRICAL RESISTANCE OF LITHIUM

Pressure, kg./cm.^{2}	0	2500	5000	10,000	15,000	20,000	25,000	30,000
R/R_0 30°C.	1·000	1·0175	1·0354	1·0727	1·1117	1·1524	1·1949	1·2394
R/R_0 75°C.	1·000	1·0172	1·0351	1·0730	1·1131	1·1553	1·1992	1·2453

Frank[142] has explained the abnormal positive pressure coefficient of resistance on the wave mechanical theory of the structure of lithium.

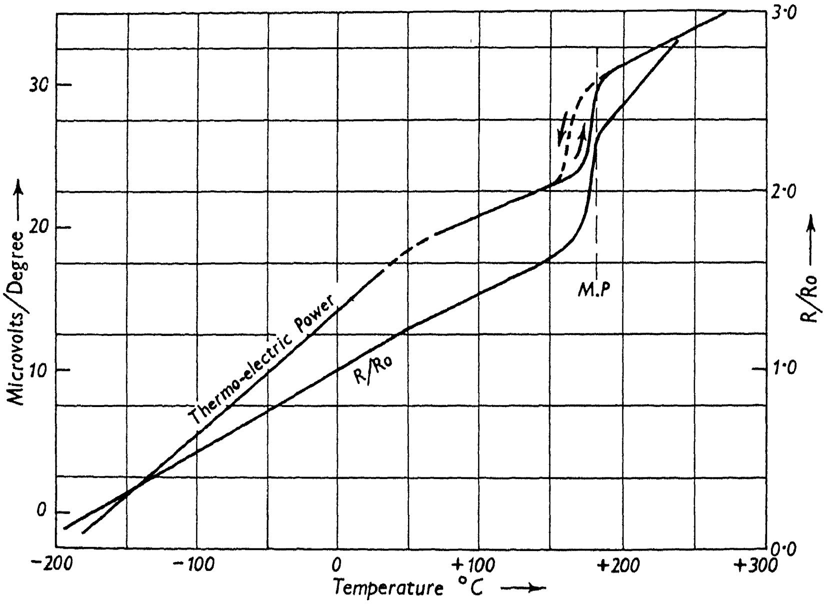

Fig. 1. VARIATION OF RELATIVE ELECTRICAL RESISTANCE AND THERMOELECTRIC POWER OF LITHIUM WITH TEMPERATURE

Although abnormal in having a positive pressure coefficient of resistance, lithium shows a normal behaviour towards tension.[66] The tension coefficient of resistance, *i.e.* the proportional change of resistance under a tension of 1 kg./cm^2, is +4·8 × 10^{-5}. Using Richards[67] values of cubic compressibility, the tension coefficient of specific resistance has been calculated as +1·1 × 10^{-5}.[66]

A transverse magnetic field of 300 kilogauss increases the resistance of a lithium wire at room temperature by less than 2%; at 88°K. the same field results in a 15% increase.[143]

The electrical resistance of lithium vapour produced by electrically exploding a wire of the metal has been compared with that of other metal vapours produced in the same way: lithium vapour showed a lower resistance than the vapours of more noble metals such as copper, silver, gold, nickel, tungsten, zinc, aluminium and tin.[144]

Thermoelectric and Photoelectric Properties

The thermoelectric power of lithium has been measured relative to platinum over the range −180° to +285°C.[18] Interpolated values are:-

t, °C.	−150	−100	−50	0	+50	+100	+150	+200	+250
Microvolts per degree	+1·5	5·5	10	14	18	21	23	31·5	34

There is a change in the slope of the thermoelectric power–temperature curve at +50°C., and there is also a marked rise of about 6 microvolts per degree in the thermoelectric power as the melting point is approached (see Fig. I). Unlike that of the other alkali metals, the thermoelectric power of the liquid lithium continues to increase with rise of temperature. More recent work has given curves for the absolute thermoelectric force and absolute thermoelectric power of lithium between 6 and 50°K.[145] There is a sharp inflexion in the thermoelectric force–temperature curve at ~30°K.: the absolute thermoelectric power is positive.

A clean lithium surface has a very low photoelectric yield which is increased by the presence of impurity molecules.[146] This fact has been used as a criterion of purity. Photosensitive films of lithium have been prepared by the evaporation of solutions of lithium in ethylamine.[147] Ives and Olpin[148] have described the preparation of photosensitive films of lithium by distilling lithium on to a tungsten surface. As the films were formed they first became sensitive to blue light, then, as their thickness increased, to green, yellow and red light: on further increasing the thickness the red and yellow sensitivity disappeared and the final thick layer was sensitive only to blue light. The photoelectric long-wave limit for the thick films approached that previously given by Pohl and Pringsheim[149] (5200 A.) and by Millikan[150] (5260 A.) for lithium metal in bulk. The wave-length of maximum excursion of the photoelectric long-wave limit coincided with the first line of the principal series (6708 A.). Lithium films on platinum were much less sensitive than those on tungsten, and this has been attributed to alloying between the lithium and platinum.[148]

The spectral characteristics of lithium–antimony photocathodes have been studied[150a-d] and their sensitivity for light of colour temperature 2360°K. has been given as 5–20 μ amp.per lumen.[150a] Multipliers with a lithium–antimony surface are particularly advantageous in scintillation counters on account of their low thermionic emission (about one fiftieth of that for caesium–antimony).[150a]

Continuous absorption of light in lithium vapour for wave-lengths in the region of the series limit has been studied and the shape of the absorption curve investigated.[150e] The absorption cross section at the series limit has been given as 2·5 × 10^{-18}cm.^{2} with an uncertainty of ± 40%. On the short wave-length side of the series limit (from 2300 A. to 1850 A.) the absorption is approximately proportional to $\lambda^{3\cdot5}$: there is a fairly steep increase over a range of 5 A. on the long wave-length side of the limit to a maximum value at 2299·6 A.

Magnetic Properties

More recent determinations of the paramagnetic susceptibility of lithium have given values considerably higher than that of 0·38 × 10^{-6} quoted previously (Mellor,II,460). A measurement by the Gouy method gave a specific susceptibility of 3·8 × 10^{-6}.[151] The Curie method has been used on thoroughly outgassed samples of lithium at field strengths from 4 to 7 kilogauss: by extrapolation to infinite field strength the effect of ferromagnetic impurities is eliminated and a susceptibility of 2·6 × 10^{-6} obtained.[152] Later measurements between 30° and 270°C. gave 2·50 × 10^{-6} at 30°C.: with increase of temperature the specific susceptibility rose slightly to 2·57 × 10^{-6} at the melting point, after which it dropped abruptly to 2·42 × 10^{-6} and then increased only slightly with further rise of temperature.[153] From other measurements between 13·9° and 300°K. the volume susceptibility (per c.c.) was represented by $\kappa \times 10^{-6} = 1{\cdot}90 + 7{\cdot}8/T$.[154] The major part of the temperature dependent term may, however, have been caused by dissolved iron present as an impurity. Computation of the volume susceptibility of lithium from a knowledge of the electronic structure has given 3·32 × 10^{-6} made up as follows:[155,156] spin paramagnetism, 3·54; free electron diamagnetism, −0·17; ion core diamagnetism, −0·05 (all × 10^{-6}). The theoretical treatment indicates an increase in the paramagnetic susceptibility of pure lithium with decrease of temperature.

Electron spin resonance absorption has been observed in bulk and dispersed lithium.[156 a-f] Line widths and shapes, relaxation times and splitting factors (*g*-factors) have been determined. From electron spin resonance studies, that part of the volume susceptibility arising from polarization of conduction electron spins has been measured as 2·0 × 10^{-6} ± 0·3 × 10^{-6}c.g.s. units.[156e] A theoretical spin susceptibility of 1·87 × 10^{-6} was calculated by Pines.[156g]

Numerous attempts have been made to evaluate the contribution of the lithium ion to the diamagnetism of its salts both from experimental data and from theoretical considerations. There are, however, wide divergencies among the recorded values, mainly as a result of differing treatments. Values given for the susceptibility of the lithium ion in solution from measurements on lithium salts include −4·0,[157] −3·3,[158] −2·9,[159] −1·6[160] and +0·3[161,162] (all × 10^{-6}). Several wave-mechanical treatments have given a value about −0·7 × 10^{-6} for the free lithium ion.[163-167] Other values for the free ion include −4·4,[158] −3·8[159] and −1·29[168] (all × 10^{-6}). In a review of the field, Klemm[169] has given +3·0 × 10^{-6} as the most probable value for the susceptibility of the Li^+ ion in solution, −0·6 × 10^{-6} for the Li^+ ion in crystals and −0·7 × 10^{-6} for the free ion. Another contemporary survey[170] recommends −1·0 × 10^{-6} for the Li^+ ion but does not distinguish between the ion in solution and in crystals.[171] Several authors have reviewed methods of obtaining ionic susceptibilities and the values resulting from them.[169,170,172,173]

From the deflexion pattern which results when a beam of lithium atoms is passed through a non-homogeneous magnetic field (the Stern–Gerlach experiment) the magnetic moment of lithium is 9·16 × 10^{-2} gauss cm.[174,175] This corresponds very closely to one Bohr magneton. Measurements by the magnetic resonance absorption method have given the nuclear moment of ^7Li to be 1·165827 ± 0·000060 times that of the proton.[176,177] Taking the moment of the proton as 2·79 nuclear magnetons, this result agrees with other precise measurements of 3·25 to 3·26 nuclear magnetons for ^7Li.[178-180] Several other determinations have given values between 3·2 and 3·3 nuclear magnetons.[181-183]

Other aspects of the nuclear moment of ^{7}Li have been discussed by a number of authors.[187-202] Of several values for the magnetic moment of the ^{6}Li nucleus[178,179,203] the best is 0·8213 nuclear magnetons.[179] Quadrupole moments of lithium have been studied.[202b,202c,203a-g] The nuclear spin is 3/2 for ^{7}Li[179,181] and 1 for ^{6}Li.[179]

As with other metals, the nuclear magnetic resonance frequency of lithium in the metallic state is greater than in its non-metallic compounds.[184-186d] Knight[186a] gave the resonance shift $\Delta H/H$ at room temperature as $0{\cdot}02 \times 10^{-2}$. More recently the resonance shift for ^{7}Li has been given as $0{\cdot}0261 \times 10^{-2} \pm 0{\cdot}0002 \times 10^{-2}$ with respect to a liquid ammonia solution of lithium nitrate.[186b] The value was constant within the experimental error of $0{\cdot}0002 \times 10^{-2}$ between room temperature and 200°C. – a range which includes the melting point of lithium.[186c] Magnetic resonance absorption line shapes and widths have also been studied.[186b-d] Over a 50° temperature range centred at 255°K. the line width narrows with increasing temperature from 6·2 gauss to approximately 0·1 gauss.[186b]

Electrode Potentials

The investigations of Lewis and co-workers on alkali metal amalgams gave -2·957 V. for the standard electrode potential of lithium (on the hydrogen scale) in aqueous solution at 25°C.[204] From free energy data, a value of -3·045 V. is obtained for the same system.[205] This comparatively large discrepancy between the experimental and calculated values has not been accounted for.[205] Recent surveys[206,207] of electrode potentials have given the mean (3·01 V.) as the best value. Determinations of the alkali metal potentials from the decomposition potentials of their fused halides have included -2·091 V. for the potential of lithium extrapolated to 18°C.[208] A value of +0·8 V. for the absolute electrode potential of the lithium ion has been calculated from spectroscopic and thermodynamic data.[209]

The potential of the ionic double layer has been calculated for lithium as –0·69 V., from which a value of –2·33 V. has been given for the potential of zero charge (or of the maximum of the electrocapillary curve).[209a]

In various non-aqueous solvents the standard electrode potential of lithium is very little different from that in water. At 25°C. the standard potential of lithium in ethyl alcohol has been determined as -3·042 V.[210] and in methyl alcohol as -3·095 V.[211] In liquid ammonia at -50°C. the standard electrode potential is -2·99 V.[212,213] Other electrode potential measurements have been made in liquid ammonia,[214] *iso*amyl alcohol,[215] hydrazine[216] and anhydrous formic acid.[217] In Table XII the electrode potentials of the alkali metals in a number of non-aqueous solvents are compared using the data of Pleskov;[216,217] the potential of the rubidium electrode in each of the solvents is arbitrarily taken as zero.

TABLE XII.- ELECTRODE POTENTIALS IN NON-AQUEOUS SOLVENTS (RELATIVE TO Rb = 0 IN EACH SOLVENT)

Element	Solvent			
	NH_3 -50°C.	N_2H_4 25°C.	H.COOH 25°C.	H_2O 25°C.
Li	-0·31	-0·19	-0·03	-0·09
Na	+0·08	+0·18	+0·03	+0·22
K	-0·05	-0·01	+0·09	+0·01
Cs	-0·02	-	+0·01	-

Values for the electrode potential of lithium relative to that of other metals in various fused halide electrolytes have been obtained by direct measurement or by calculation from thermodynamic data.[217a–b] Electrochemical series have been developed, the order of the metals varying with the temperature and with the nature of the anion.

The behaviour of lithium ions at the dropping mercury electrode has been investigated in both aqueous and non-aqueous media. Lithium was among elements studied by Heyrovsky[218,219] in his first polarographic experiments; he gave the deposition potential of lithium at mercury from aqueous solutions as −2·03 V. relative to a normal calomel electrode. Despite the very negative standard potential of lithium, its ions are discharged at a mercury electrode in neutral and alkaline solutions on account of (*a*) compound formation between lithium and mercury, and (*b*) the high hydrogen overvoltage at mercury. The negative potential does, however, limit the choice of supporting electrolyte; tetra-alkylammonium halides or hydroxides are virtually the only usable salts.[220] With tetramethylammonium chloride or hydroxide as the supporting electrolyte, the half-wave potential of lithium ions in aqueous solution at 25°C. has been given as −2·31 V.[221,222] and $-2{\cdot}38_5$ V.[222a,222b] relative to a normal calomel electrode. In 0·1 M-tetra-*n*-butylammonium hydroxide at 25°C. it has been given as −2·331 ± 0·003 V. against a saturated calomel electrode (equivalent to −2·3 V. against a normal calomel electrode).[222c] The diffusion current of lithium in aqueous solution is, however, very ill-defined:[223] alcohol-water mixtures give better results. In 50% ethyl alcohol at 25°C., with 0·1 M-tetraethylammonium hydroxide as the supporting electrolyte, the half-wave potential of lithium is −2·31 V. relative to a saturated calomel electrode:[224,225] in 80% ethyl alcohol the potential is slightly less negative. The half-wave potential of lithium is sufficiently removed from those of the other alkali metals (Na, −2·07; K, −2·10; Rb, −1·99; Cs, −2·05; all in 50% ethyl alcohol +0·1 M-tetraethylammonium hydroxide) to permit separate determination of the lithium ion.[218] In liquid ammonia at −36°C. saturated with tetrabutylammonium iodide as supporting electrolyte, the half-wave potential of the lithium ion relative to a 0·1 N. $Pb/Pb(NO_3)_2$ reference electrode is −1·67 V.[226] Other polarographic studies have been made in methyl alcohol and in methyl alcohol-benzene and methyl alcohol–water solutions.[227]

Ionization Potentials, Electron Affinity and Electronegativity

Precise values for the three ionization potentials of lithium have been calculated from spectral series limits. Values, in electron volts, from two recent compilations are:-

I	II	III	Reference
5·39	75·62	122·42	228
5·40	75·7	121·8	229

Several other experimental methods[230–233] have been used to determine ionization potentials of lithium, and a number of theoretical treatments have been given.[23,24,27,234–240]

Estimates of the electron affinity of lithium obtained by quadratic extrapolation from the ionization potentials of isoelectronic species are 0·34,[241] 0·47[242] and 0·38 e.V.;[243] the last value is derived from the latest spectroscopic data. It has been suggested[242] that values obtained by such procedures are to be regarded as lower limits. A linear extrapolation method,[244] which in general yields less satisfactory values, gives 0·7 e.V. for the electron affinity of lithium.[243] Using a wave-mechanical variational method, Wu[245] calculated 0·54 e.V. for the electron affinity of lithium in its normal state.

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More recently, a value of 0·74 e.V. has been calculated using the Ritz variational method in conjunction with an extrapolation procedure.[246] The positive electron affinity shows the negative Li^- ion to be stable. Such ions have been produced by bombarding nickel surfaces with Li^+ ions.[247]

On Pauling's electronegativity scale lithium has a value of 1·0, values for the other alkali metals being Na, 0·9; K, 0·8; Rb, 0·8 and Cs, 0·7.[33] Mulliken[248] has pointed out that the average of the first ionization potential and the electron affinity of an atom should give a measure of its electronegativity: the sum of the ionization potential and the electron affinity divided by 130 gives values in close agreement with Pauling's electronegativity both for lithium and other atoms.[33]

Miscellaneous Physical Properties

From nuclear magnetic resonance measurements[186d] the coefficient of self-diffusion in lithium has been given as:-

$$D(\text{cm.}^2/\text{sec.}) = 0{\cdot}24 \begin{smallmatrix} +\ 0{\cdot}17 \\ -\ 0{\cdot}10 \end{smallmatrix} \exp(-13{,}200 \pm 400/RT)$$

Earlier nuclear magnetic resonance experiments[186b] led to 9·8 ± 1 kg.-cal./g. atom for the activation energy of self-diffusion whilst from the anomalous rise of electrical resistance that starts well below the melting point it has been estimated[248a,b] as 9·3 ± 0·35 kg.-cal./g. atom.

The coefficient of diffusion of lithium in mercury at 8 to 15°C. calculated[249] from the atomic radius and viscosity data using the Stokes–Einstein equation is 0·72 cm.^{2} per 24 hours. This is in reasonable agreement with the older experimental figure of 0·66 cm.^{2} per 24 hours (Mellor,II,456).

Metallic lithium heated on the surface of germanium and silicon crystals diffuses rapidly into the crystals and acts as a strong donor element.[249a-c] Diffusion constants have been obtained by a method involving the measurement of p-n junction positions[249a] and also by measuring the mobility of the Li^+ ion and applying the Einstein relation between diffusion constant and mobility.[249b,c] The latter method which is considered to be capable of greater accuracy has given:[249c]

$$\begin{aligned} &D(\text{cm.}^2/\text{sec.}) = 0{\cdot}0025 \exp(-11{,}800/RT) \text{ for germanium } (150\text{–}600°\text{C.}) \\ \text{and } &D(\text{cm.}^2/\text{sec.}) = 0{\cdot}0023 \exp(-15{,}200/RT) \text{ for silicon } (360\text{–}860°\text{C.}) \end{aligned}$$

When sealed tubes made of 1 mm. wall 0·1% carbon steel and containing lithium are heated in hydrogen it is reported that carbon inclusions in the steel are reduced by the hydrogen forming voids through which the lithium seeps out.[249d] Lithium does not permeate gamma steel or pure iron. Also quenched steels remain impermeable to lithium on heating at 600°C. in hydrogen because of the fine distribution of carbides.[249d]

Alkali halide crystals heated in contact with lithium vapour undergo additive colouration as they do with other alkali metals.[249e]

An approximate value of 3000 m./sec. has been obtained for the velocity of ultrasonic waves (12 Mc/sec.) in liquid lithium at 200°C.[249f]

Calculated values for the Hall coefficient of lithium, −0·00135[250] and −0·00137 c.g.s.,[251] are somewhat lower than an earlier experimental value (−0·0017 c.g.s.).[252]

Thin films of lithium, like those of the other alkali metals, are opaque to visible light but are highly transparent in the ultra-violet region of the spectrum.[252a,b] The wave-length at which an alkali metal ceases to exhibit the optical properties of a metal and acquires that of a transparent medium decreases with decreasing atomic number and for lithium lies between 1550 A.[252b] and 2050 A.[252a]

The contact potential difference between lithium and barium surfaces, prepared by condensing their vapours on glass, has been measured as 0·03 ± 0·02 V., lithium being electropositive to barium.[253] This result has led to the value 2·49 ± 0·02 e.V. for the work function of lithium. Klein and Lange[254] have obtained the electron work functions of a large number of metals from potential measurements on amalgam systems: their values include 1·40 e.V. for lithium.

Lithium shows no natural radioactivity.[255]

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PROPERTIES OF THE LITHIUM ION

Some properties of the lithium ion, and some properties that relate to both the metal and its ion, have been dealt with under the appropriate sections above. Other properties of the Li^+ ion will be considered here.

The Ion in Solution

The heat and free energy of formation of the aqueous lithium ion at 25°C. are −70·22 and −66·554 kg.-cal.g.ion^{-1} respectively.[1] Assuming equal values for the heat capacities of the NH_4^+ and Cl^- ions, the absolute heat capacity of the lithium ion at infinite dilution has been calculated as −9·9 g.-cal./degree/g.-ion.[1a] From thermal data for the ionization process Li_2CO_3 (solid) $\rightarrow$ $2Li^+$ (aq.) + CO_3^- (aq.), Latimer *et al.*[2] obtained 4·7 ± 1·0 g.-cal.g.-ion^{-1} degree^{-1} for the entropy of the Li^+ ion (relative to that of the H^+ ion) in aqueous solution at 25°C. The Bureau of Standards selected value for the entropy of the aqueous lithium ion at 25°C. is 3·4 g.-cal.g.-ion^{-1} degree^{-1}.[1]

Kielland[3] used a variety of methods to calculate the effective diameter of the hydrated lithium ion, and then, taking a rounded value of 6×10^{-8} cm. for this dimension, used the Debye–Hückel theory to compute the activity coefficients of the lithium ion in aqueous solution at 25°C. shown in Table XIII.

TABLE XIII. - ACTIVITY COEFFICIENTS OF THE Li^+ ION IN AQUEOUS SOLUTION AT 25°C.

Total ionic concentration	0·001	0·002	0·005	0·01	0·02	0·05	0·1	0·2
Activity coefficient	0·975	0·965	0·948	0·929	0·907	0·87	0·835	0·80

The indefinite significance of ionic solvation numbers has been discussed by Bockris[4] who has distinguished between 'primary solvation' – where (*a*) the ion and its attached solvent molecules move as one entity during electrolytic transport, and (*b*) the solvent ions have completely lost their own separate translational degrees of freedom – and 'secondary solvation' which refers to all electrostatic interactions not included in the foregoing definition of primary solvation. Experimental methods which are believed to measure primary hydration numbers, viz. those employing ionic mobility, ionic entropy, compressibility and partial molar volume, give values of 5, 5, 3 and 2 respectively for the hydration of the lithium ion.[4] Using a dialysis method, it has been reported that five water molecules are bound to the Li^+ ion forming a complex aquo-metal ion and that a further ten water molecules are bound as water of hydration of the aquo-metal ion.[5] Samoilov[6] has criticized the concept of fixed ionic hydration numbers and definite Stokes' radii on the grounds that the time of stay of water molecules around ions is not markedly greater than in pure water. From viscosity and mobility data he has shown that even for the strongly hydrated lithium ion there can be no permanent binding of water since the time of stay of water molecules around the Li^+ ion is only twice that around molecules in a pure water medium. Solvation of lithium ions in such liquids as methyl and ethyl alcohol, acetone, acetonitrile and benzonitrile has been considered.[7] In water–alcohol mixtures the lithium ion is said to be solvated by alcohol pentahydrate molecules as well as by water and alcohol molecules.[8]

Independent treatments by Latimer and co-workers[9] and by Verwey[10] have led respectively to values of 121·2 and 120 kg.-cal.g.-ion^{-1} for the heat of hydration of the Li^+ ion, to 114·6 and 112·5 kg.-cal.g.-ion^{-1} for the free energy of hydration, and to 22 and 24·5 g.-cal.g.-ion^{-1} degree^{-1} for the entropy of hydration. In an earlier treatment, Bernal and Fowler[11] by two different methods calculated values of 136 and 131 kg.-cal.g.-ion^{-1} for the heat of hydration of the Li^+ ion. Whereas Bernal and Fowler assumed approximately equal heats of hydration for the equi-radial K^+ and F^- ions, Miscenko[11a] has ascribed equal heats of hydration to the Cs^+ and I^- ions on the grounds that the difference in their radii is compensated by the dipole moment assymetry in the water molecule. In this way he obtained 121 kg.-cal.g.-ion^{-1} for the heat of solvation of the Li^+ ion. Elsewhere, Miscenko[12] again using thermochemical data on the solvation of salts, has given the heat of solvation of the Li^+ ion in water as 125 kg.-cal.g.-ion^{-1} and in methyl and ethyl alcohols as 127 kg.-cal.g.-ion^{-1} From the Bjerrum equation for solvation, the same author calculates values of 240, 243 and 246 kg.-cal.g.-ion^{-1} for the heats of solvation of Li^+ in water, methyl alcohol and ethyl alcohol respectively; and from the Born equation for solvation he calculates 236, 231 and 229 kg.-cal.g.-ion^{-1} for the solvation energies in the same three solvents.[12] These calculations do, however, involve a number of dubious assumptions.[13]

A recent compilation[14] of ionic mobilities, using conductivity and transport number data from a number of sources, gives the values in Table XIV for the equivalent conductivity or mobility of the lithium ion at infinite dilution in water.

In heavy water at 25°C. the mobility of the lithium ion at infinite dilution is 30·93 and the transference number of the Li^+ ion in lithium chloride solution is reported to decrease by about 2% on passing from H_2O to D_2O.[15] In methyl alcohol the mobility of the lithium ion at infinite dilution is 39·82 at 25°C.,[16] while in ethyl alcohol it is 15·00 at 25°C. and 9·62 at 4°C.[17] Other values for ethyl alcohol–water mixtures at 25°C. are:-[13,18]

TABLE XIV.- MOBILITY OF THE LITHIUM ION AT INFINITE DILUTION IN WATER

Temp. °C.	0	5	15	18	25	35	45	55	100
λ_∞	19·4	$22{\cdot}7_6$	$30{\cdot}2_0$	32·8	$38{\cdot}6_8$	$48{\cdot}0_0$	$58{\cdot}0_4$	$68{\cdot}7_4$	115

Mol. % EtOH	5	10	15	20	30	40	60	80
λ_∞	26·7	19·9	16·7	15·2	14·0	13·8	14·7	15·8

A considerable amount of data exists for the conductivity of lithium salts in other non-aqueous solvents, but there is little corresponding transport number data to permit the calculation of precise ionic mobilities. Mobilities of the lithium ion in a wide range of non-aqueous solvents have, however, been obtained[7,19] with the aid of such relationships as that between conductivity and viscosity (Walden's rule). The heat of transport[20] and entropy of transport[21] for the Li^+ ion have been discussed.

Diffusion coefficients at infinite dilution may be obtained from the above mobility data by using the equation:[22] $D = 8{\cdot}93T \times 10^{-10}\ \lambda_\infty$ cm^{2}sec^{-1}. This leads to $1{\cdot}03 \times 10^{-5}$ cm^{2}sec^{-1} for the diffusion coefficient of the lithium ion at infinite dilution in water at 25°C. The temperature dependence of the diffusion current of Li^+ ions at the dropping mercury electrode has been calculated.[23]

From measurements of the viscosity of mixed electrolytes in aqueous solution a value of 0·0087 has been calculated for the specific viscosity of the Li^+ ion in 0·1 N.solution.[24] Relationships between the viscosity, the mobility and the entropy of hydration of the lithium ion have been discussed.[25]

The extensive work of Okazaki on the Faraday effect in aqueous salt solutions has led to the following values for the magneto-rotatory power of the lithium ion (in min.cm^{2}gauss^{-1}g.-ion^{-1}), a value of zero being assumed for the hydrogen ion:-[26]

Wave-Length, A.	5900	5500	5100	4700	4300	3900	3500
$[M]$	0·15	0·15	0·17	0·18	0·21	0·26	0·34

Okazaki[27] has also defined a molecular magnetorotation constant, $\Phi = Mnw\lambda^2/$

$s(n^2 + 2)^2$, where n and w are respectively the refractive index and Verdet's constant for light of wave-length λ, M is the molecular weight and s the density: the constant is the sum of the Φ values for the constituent ions. For the lithium ion, Φ has a value of $-0{\cdot}68 \times 10^{-14}$: values for other ions include Na^+, $-0{\cdot}23$; K^+, $0{\cdot}61$; H^+, $-1{\cdot}41$; F^-, $1{\cdot}57$; Cl^-, $11{\cdot}17$; Br^-, $19{\cdot}58$.

The refractivity of the lithium ion in aqueous solution for the sodium *D*-line is $-0{\cdot}42$.[28]

Exchange of lithium ions with other ions has been studied in a variety of synthetic ion-exchange resins[28a-q] as well as in natural exchangers such as minerals.[28r-w] Exchange systems to receive attention have included Li-H,[28f,28j-p,28r,28u] Li-Na,[28m,28v] Li-K,[28l-m] Li-Mg,[28s] and Li-Ag.[28n,28v] The strength of binding of an ion by an exchanger depends on the charge of the ion and on its hydrated radius. For ions of equal charge the binding increases with decreasing hydrated radius, and in dilute solutions the adsorption affinities or exchange affinities of alkali metal ions follow the series $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.[28a,c,r] Several specialist books may be consulted for further information on ion-exchange and its applications.[28x-z] [29]

The Gaseous Ion

Lithium ions can be produced by heating lithium compounds on a wire filament. A study of the emission from sources of various composition has indicated that the silicate $Li_2O,Al_2O_3,2SiO_2$ is the most satisfactory ion emitter.[30] The naturally occurring mineral spodumene, having a composition approximating to the above, has been used by a number of workers. An electron multiplier tube has been used for counting single lithium ions.[30]

Ionic microscopy has been carried out[30b-e] using lithium ions, and replacement of the electron source in an industrial electron microscope by a thermal Li^+ ion source has been described.[30d] Although theoretically Li^+ ions are capable of a higher resolving power than are electrons at the same accelerating voltage, the resolution in Li^+ ion images of oxide smokes obtained by Gauzit[30d] was lower than in electron images because of disturbing side effects and greater experimental difficulties. Lithium ions tend to destroy the object more than do electrons, and they can form deposits on it after a time.

At 0° and 298·16°K. the U.S. Bureau of Standards selected values for the heat of formation of the gaseous lithium ion are 160·799 and 162·860 kg.-cal. g.-ion^{-1} respectively.[1]

The mobility (in cm./sec./volt/cm.) of the Li^+ ion in various gases at 760 mm. and 20°C. is as follows:-[31]

He	Ne	A	Kr	Xe[32]	H	N
25·3	14·35	4·99	4·03	3·04	13·3	4·21

Other measurements[32] in helium, neon, argon and krypton are in fairly close agreement with the above. The temperature variation of the mobility in helium has been determined over the range 20·5 to 483°K.,[33] and mobility measurements have also been made in argon-xenon and helium-xenon mixtures.[34] A theoretical calculation employing the exchange force between lithium ions and helium has given 194 cm./sec./volt/cm. for the mobility of the Li^+ ion in helium.[35] In the presence of water vapour, alkali metal ions acquire a cluster of water molecules which reduces their mobility. The mobility of the Li^+ ion has been studied in all five of the rare gases containing small concentrations of water vapour, and the values are found to be about half those in the absence of water vapour.[32] In argon, krypton and xenon an upper limit of six has been assigned to the number of water molecules in an ion cluster, but the true number is probably less than this.

Measurements have also been made in pure water vapour.[36] Under conditions of low field/pressure ratio and low temperatures, all the inert gases may attach themselves to the Li^+ ion.[37] The number of attached inert gas atoms decreases with rise of temperature, and for a given temperature it increases along the series: He, Ne, A, Kr, Xe. Thus, in neon practically all the Li^+ ions show attachment at 90°K. but there is no attachment at 195°K. In argon the corresponding temperature limits are 195°K. and 290°K., while in xenon and krypton every ion collects at least one and probably two gas atoms at room temperature.

A good deal of work has been reported on the ionization of the inert gases by lithium and other alkali metal ions.[38-46] Beeck and Mouzon[41,42] found that, in general, an inert gas is most easily ionized by the alkali ion nearest to it in the periodic system. The potentials (ion velocities) required by Li^+ ions for them to ionize Ne, A, Kr and Xe were determined as 307, 100, 420 ± 10 and 250 V., respectively. Later work by Varney,[46] using a space-charge method sensitive to any resulting positive ions but not affected by secondary electrons liberated from the walls, revealed no ionization of the inert gases by Li^+ ions, and it has been suggested that the interference of secondary electrons may have been responsible for the results of Beeck and Mouzon. Scattering of lithium ions by metal vapours has been studied.[47,48]

Lithium ions can migrate through quartz plates in an electric field.[49,50] It is thought that migration takes place through tunnels inherent in the crystal structure and parallel to the principal axis of the quartz.[50,50a] Studies have also been made of the reflexion of lithium ions from metal surfaces.[51-54c] When the metals are given a coating of salts etc., the bombardment by lithium ions gives rise to negative ions.[53] Negative ions can also result from metal surfaces alone owing to the presence of adsorbed gases etc.[53] Negative lithium ions have been detected using such techniques.[55]

The ionic refractivity of the gaseous lithium ion for the sodium *D*-line is 0·20.[28] Values for the polarizability of the lithium ion include 0·075,[56] 0·0313[57] and 0·025[58] (all × 10^{-24}). Other dielectric parameters of the lithium ion have been evaluated.[59-61]

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SOLUTIONS OF LITHIUM

Solutions of Lithium in Liquid Ammonia

Lithium dissolves readily and without reaction in liquid ammonia to give solutions which are blue when dilute. Concentrated solutions of alkali metals in ammonia show metallic reflexion, and according to Jaffe[1,2] the light reflected from a saturated solution of lithium in ammonia changes from deep red to yellow, green and finally white as the angle of incidence is increased from 0 to 90°. The absorption spectrum of the dilute solutions shows a single broad band with a maximum around 6700 cm.$^{-1}$ and a half-height width of about 3000 cm.$^{-1}$.[2a]

There is a slight increase of solubility with temperature from 10·698 g. of lithium per 100 g. of ammonia at −63·5°C. to 11·319 g. of lithium per 100 g. of ammonia at 0°C.[3] An earlier measurement at −39·4°C. gave 11·3 g. of lithium per 100 g. of ammonia.[4] All these solubility figures were obtained by studying vapour pressure–composition curves; an older direct determination gave a constant solubility of 10·3 g. of lithium per 100 g. of ammonia between −80° and 0°C.[5] The heat of solution becomes more negative with increasing lithium concentration and thus heat absorption occurs on dilution. When each lithium atom is dissolved in 102·8 moles of ammonia, the heat of solution is −79·6 kg.-cal. per atom of lithium: for one lithium atom in 20·9 moles of ammonia it is −8·38 kg.-cal.[6] Other measurements in dilute solutions have given −8·0[7] and −9·6 kg.-cal.[8] per g. atom of lithium. The high heat of solution has been attributed, in part, to the formation of an ammoniated metal ion.[6]

Density values for solutions of lithium in liquid ammonia at −33·2°C., are given in Table XV;[9] other determinations[10] at −35°C. are in close agreement with these ($d = 0{\cdot}5435$ for 13·5 mole % Li to 0·4920 for 21·0 mole % Li). For saturated solutions the density varies from 0·477 ± 0·006 at +19°C. to 0·495 ± 0·006 at −80°C.: the mean coefficient of expansion between −80° and +19°C. is 0·00036 ± 10%.[1] On solution there is an increase in the volume of

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TABLE XV. - DENSITY OF SOLUTIONS OF LITHIUM IN LIQUID AMMONIA AT −33·2°C.

Mole Fraction Li	0·0331	0·0571	0·0713	0·1180	0·1557	0·1616	0·1958	0·2105 (satd.)
Density	0·639	0·611	0·597	0·554	0·523	0·518	0·498	0·490

the system, and at high lithium concentrations the density of the solution is less than that of either of the consituents. At −35°C. the volume increase on solution varies linearly from 37·5 c.c. per g.-atom of lithium for a saturated solution to 41·4 c.c. for 1 g.-atom of lithium dissolved in 6·4 moles of ammonia.[10] A saturated solution of lithium in ammonia is the lightest liquid known at room temperature.[1]

Sound-velocity measurements have shown the adiabatic compressibility of concentrated solutions of lithium in ammonia to increase rapidly with increasing metal concentration.[10a] At 40 moles NH_3/g.-atom Li the compressibility was 55×10^{-12} cm.^{2}/dyne; at 10 moles NH_3/g.-atom Li it was 80×10^{-12} cm.^{2}/dyne.[10a]

Solutions of lithium in ammonia have a very low vapour pressure compared with that of the pure solvent. Representative values at −39·4°C. are shown in Table XVI.[4]

TABLE XVI. - VAPOUR PRESSURE OF SOLUTIONS
OF LITHIUM IN AMMONIA AT −39·4°C.

Moles NH_3/Atom Li	1·72	3·40	4·07	4·88	5·79	7·56
Pressure, mm.Hg.	3·50	3·70	134·80	281·70	395·50	474·80
Moles NH_3/Atom Li	10·97	15·08	21·33	30·81	45·66	60·13
Pressure, mm.Hg.	520·30	534·10	538·70	543·60	539·70	549·60

Other measurements have been made at higher and lower temperatures.[3,11] For a saturated solution the vapour pressure reaches one atmosphere at about +63°C.[12]

The nature of lithium solutions in liquid ammonia has been the subject of much discussion and controversy. Early workers considered that alkali metals dissolve in liquid ammonia to give true compounds in which the metal is joined directly to the nitrogen atom of the ammonia forming a substituted ammonium radical,- and the term 'metal ammonium' was employed. But according to Kraus and Johnson,[4] while lithium atoms (or ions) may be associated with molecules of the solvent, there are no grounds for considering that in ammonia solutions there is a molecular complex resembling the ammonium group and they have condemned the term 'metal ammonium'. The vapour pressure curve obtained by these workers was entirely regular with no indication of the irregularities observed by Benoit[11] from which the formation of a compound $Li,4NH_3$ or $Li_2,8NH_3$ had been deduced. A detailed review of work on the nature of alkali metal solutions in liquid ammonia with numerous references up to 1931 has been given by Johnson and Meyer.[13] Fernelius and Watt[14] have also reviewed the subject.

A study of the lithium-ammonia system below the freezing point of ammonia, −78°C., has shown a progressive depression of freezing point with increasing concentration of lithium, although there is a considerable departure from Raoult's law.[15,16] At the eutectic temperature, −181 ± 3°C.,[1] −185°C.,[15,16] compound formation appears to occur, solvation of the lithium being carried over into the solid state to give a lithium ammoniate containing not more than 4 ammonia molecules for each lithium atom.[15-17] The solid is bronze-coloured and its low resistivity, 15×10^{-6} ohm cm., is a quarter of that for the saturated liquid phase.[1] Thin layers of the solid are blue by transmitted light.[16] A light absorption band at 1·15 μ has been observed in thin layers of ammonia containing small amounts of lithium, sodium or potassium at 20°K.[17a] This is independent of the nature of the alkali metal but there are further bands characteristic of the actual alkali metal employed; for lithium-ammonia layers at 20°K. an absorption band occurs at 585 mμ.[17a]

Dilute solutions of lithium in ammonia show an electrical conductivity behaviour similar to that of ordinary electrolytes, the equivalent conductivity approaching a limiting value with increasing dilution.[18] At a concentration of approximately 0·05 N. the equivalent conductance is a minimum ($\sim$450 ohms^{-1}) and thereafter it increases rapidly with increasing concentration ($\sim$900 ohms^{-1} at 0·5 N. and 125,000 ohms^{-1} at 2·3 N.). In concentrated solutions the electrical conduction is similar to that in metals.[1,18] At −80° the specific resistance of a saturated solution is $0{\cdot}64 \times 10^{-4}$ ohm cm.; the temperature coefficient of resistance between −80 and −120°C. is −0·02%.[1] According to Kraus[18,19] there exists in ammonia solutions the equilibrium $Li \rightleftharpoons Li^+ + e^-$, the positive carrier being the normal lithium ion while the negative carrier is the electron, which may be associated with one or more ammonia molecules. With increasing metal concentration the solvation of the electron decreases until eventually some carriers become free from ammonia molecules. It is the presence of these free electrons which is responsible for the metallic conduction at high concentrations. In dilute solutions, where the solvation of the electrons reduces their mobility, an appreciable part of the current is carried by the Li^+ ion, and the relative decrease in the number of carriers with increasing total lithium concentration results in a decrease in equivalent conductivity with increasing lithium concentration. While this theory gives a satisfactory account of the conductance behaviour it meets some difficulties in other directions.[20] More recently it has been proposed that the electrons are trapped in the solvent, there existing in the liquid cavities which serve to trap electrons singly or in pairs.[20 a–c] Several other authors[2a,20 d–h] have discussed and elaborated the model. A study of electrical conductivities and solubility relationships in the system lithium-sodium-ammonia[21] has shown that in dilute ammonia solutions the conductivities of lithium and sodium are practically additive.

A sharp rise in the resistivity of a solution containing ammonia and lithium in the ratio 15·5:1 when the temperature is lowered below −60°C. appears to indicate that separation into two phases occurs at this temperature.[22] At −70°C. two phases are clearly visible, the upper layer being bronze-coloured and the lower deep blue.

Photoelectric activity has been observed in solutions of lithium in liquid ammonia.[18] The Hall effect has been investigated in solid and liquid lithium-ammonia solutions.[1] The effect of a magnetic field on the electrical resistance of the solid has also been studied.[1]

The decomposition of ammonia solutions and the reactions of lithium dissolved in ammonia are discussed later (see page 87).

Other Solutions of Lithium

Solutions of lithium in solvents other than liquid ammonia have been given very little attention. This is doubtless due, at least in part, to their poor stability. Lithium is reported to be soluble in methylamine,[2a,23–27a] ethylamine[2a,28–29a] and ethylenediamine,[14,26] and to be slightly soluble in hydrazine.[30] The solutions are mostly blue and they deteriorate quite rapidly.[14,26,27] Two liquid phases have been reported in the lithium–ethylamine system at 0°C.;[29a] one is blue and the other colourless, the colourless phase being very slightly the denser. Lithium is insoluble in propylamine and in secondary and

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tertiary amines.[28] Solutions of lithium in methylamine (at −55°C.) and in ethylamine (at −40°C.) show broad light absorption bands at about 7600 cm.$^{-1}$ and 7000 cm.$^{-1}$ respectively.[2a] Paramagnetic resonance has been studied in solutions of lithium in methylamine and ethylenediamine.[26] Electrical conductance has been studied in concentrated solutions in methylamine.[27a]

A high solubility has been reported for lithium in its fused chloride although actual values of the solubility have not been determined.[31] The potential of a carbon electrode immersed in solutions of lithium in lithium chloride containing up to about 0·2% by weight of lithium has been studied at 650°C. and found to follow the equation[31] $E = \text{const.} - RT/F \ln [\text{Li}]$. The dissolved lithium is believed to exist in the atomic form or as the complex ion Li_2^+.

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ATOMIC WEIGHT AND ISOTOPES

The internationally accepted value (1955) for the atomic weight of lithium remains at 6·940, a figure which was based originally on determinations of the LiCl:AgCl and LiCl:Ag ratios by Richards and Willard[1] in 1910. The only more recent chemical determination[2] of the atomic weight gave a value of 6·934 ± 0·001. This was obtained by determining the ratio LiCl:AgCl using pure lithium chloride prepared from the carbonate. A value of 6·9364 ± 0·0018 has recently been calculated from density and *X*-ray data and there is some reason for believing that this may be a more realistic figure than 6·940.[3] Urey and Greiff[4] pointed out in 1935 that isotopic exchange reactions can affect the atomic weight of lithium by about 0·001 and that atomic weights given to more significant figures are meaningless unless the isotopic composition is specified. Atomic weights calculated from the isotopic masses and the natural abundance ratio of the lithium isotopes vary considerably, mainly as a result of variations in the observed values of the latter (see below). Thus, while the most reliable mass spectrographic determinations of the abundance ratio have led to atomic weights of 6·939 to 6·943,[5,6] optical determinations of the abundance ratio have led to atomic weights around 6·90.[7-9]

Shortly after the first discovery of isotopes it was shown by several workers using the methods of positive ray analysis that lithium has two isotopes of mass number 6 and 7.[10-14] Since then numerous determinations of the natural abundance ratio of these isotopes have been made using both mass spectra and optical methods. It will be seen from Table XVII that there are wide variations – from 7 to 15 – in the reported values for the $^7Li/^6Li$ ratio, and that there are fairly consistent differences between the mass spectra and optical determinations. A recent survey of abundance ratio data for lithium showed no satisfactory explanation for the disagreement between the various workers.[15] The most widely accepted values lie between 12 and 13.

TABLE XVII. - NATURAL ISOTOPIC ABUNDANCE RATIO FOR LITHIUM

Authors	$^7Li/^6Li$ Ratio	Method	References
Morand	14·9	Mass Spectrum	16,17
Bainbridge	11·28±0·07	Mass Spectrum	18
Aston	10·2–12·9	Mass Spectrum	19,20
Harnwell and Bleakney	8·4	Mass Spectrum	21
Brewer	11·6–12·52	Mass Spectrum	5,22-26
Bondy and Vanicek	12	Mass Spectrum	27
Hoff Lu	12·29±0·07	Mass Spectrum	28
White and Cameron	12·7±0·07	Mass Spectrum	6
Hintenberger	12·4–12·52	Mass Spectrum	29
Cameron	12·44–12·93	Mass Spectrum	29*a*
van Wijk	7·2	Absorption spectrum of Li_2	7,30
Nakamura	8	Absorption spectrum of LiH	8
Schüler	10·5	Atomic spectrum	31
Ornstein *et al.*	8·1±0·4	Atomic spectrum	9
McKellor and Jenkins	8·57	Absorption spectrum of Li_2	32

In measuring the abundance ratio using a mass spectrometer, Brewer[5,25] observed an isotope effect in the evaporation of lithium ions. A value of 11·6 was obtained for the $^7Li/^6Li$ ratio until the source – a platinum disc impregnated with a lithium compound – became 40% depleted. Beyond this point lower values were obtained, and after applying a correction for the isotope effect of free evaporation the $^7Li/^6Li$ ratio became 12·52. White and

Cameron[6] reduced the isotope effect of free evaporation by distilling the heavy molecule lithium aluminium chloride ($LiAlCl_4$) into the ionization region. Subsequent workers[5,18] have not supported a report[33] that the ^{7}Li/^{6}Li ratio decreases with increase of temperature. It has been reported[26] that the isotopic ratio in old mineral formations, presumed to be of marine plant origin, does not differ significantly from that in other sources. Cameron,[29a] however, has found small variations in the ^{7}Li/^{6}Li ratio of mineralogical and commercial samples of lithium compounds from various sources. In commercial samples of lithium salts the variation was between 12·44 and 12·93; in minerals it was between 12·47 and 12·72.

Mass spectroscopic evidence has been reported for the existence of ^{5}Li, with a ^{7}Li/^{5}Li ratio of 20,000±1000.[24] Later work has not, however, confirmed the existence of such a stable isotope, and lower limits of 10^5 and 10^7 have been given for the ^{7}Li/^{5}Li ratio.[6,34]

In addition to the stable isotopes ^{6}Li and ^{7}Li, other artificial lithium isotopes with short half lives have been produced in nuclear bombardment reactions. A recent review,[35] which also summarizes methods of production and disintegration schemes, lists ^{8}Li with a half life of 0·88 sec. and ^{9}Li with a half life of 0·17 sec. There is also a metastable excited state of ^{7}Li which decays by undergoing an isomeric transition and has a half life of $5{\cdot}2 \times 10^{-14}$ sec.

The earliest measurements of the precise masses of the lithium isotopes were made by Aston,[36,37] and by Costa,[38,39] who showed that they lay close to whole numbers. In 1933 Bainbridge,[40] from mass spectrographic measurements, obtained ^{6}Li = 6·0145 ± 0·0003 and ^{7}Li = 7·0146 ± 0·0006 on the physical basis of atomic weights (^{16}O = 16). Other calculations of the isotopic masses of lithium have been made from measurements of nuclear reaction energies. These include (all on the physical scale) ^{6}Li = 6·0143 ± 0·0002, ^{7}Li = 7·0148 ± 0·0002;[41] ^{6}Li = 6·01634, ^{7}Li = 7·01720;[42] ^{6}Li = 6·0170, ^{7}Li = 7·0182;[43] ^{6}Li = 6·0167, ^{7}Li = 7·0180;[44] ^{6}Li = 6·01670 ± 0·00012, ^{7}Li = 7·01799 ± 0·00011;[45] ^{6}Li = 6·01682 ± 0·00011, ^{7}Li = 7·01784 ± 0·00009.[46] Bainbridge[47] in 1948 recommended the adoption of ^{6}Li = 6·01690 as the most probable value from mass spectrograph and nuclear disintegration experiments: ^{7}Li was given as 7·01820 ± 0·00010 from mass spectrograph values only. A survey[47a] based on mass spectrographic and nuclear reaction data available up to 1952 has given ^{6}Li = 6·017028 ± 0·000006 and ^{7}Li = 7·018225 ± 0·000007; a more recent survey by Drummond[47b] has given virtually the same values.

From measurements of the isotope effect in the red region of the Li_2 absorption spectrum, Almy and Irwin[48,49] obtained a value of 1·04077 ± 0·0004 for the mass coefficient, ρ. The mass coefficient is related to the relative masses of the lithium isotopes (the mass ratio) by the expression: mass ratio = $2\rho^2 - 1$, and this leads to a value of 1·16640 ± 0·00016 for the mass ratio ^{7}Li/^{6}Li. Another determination[32] also using the red absorption bands of lithium is in excellent agreement with the above (ρ = 1·04076 ± 0·0003; mass ratio = 1·16636 ± 0·00009), and these values also agree closely with those obtained from mass spectrometric measurements[39,40] and from nuclear transformation energies.[41-46] Earlier measurements in the blue-green region of the Li_2 absorption spectrum gave higher values of 1·04141 ± 0·00008 and 1·1690 ± 0·0003 for the mass coefficient and mass ratio respectively.[50,51]

Separation of Isotopes

The only complete separations of the lithium isotopes have been performed on a comparatively small scale by employing the principle of the mass spectrograph.[17,52-55] Using as a source platinum filament coated with a mixture of the composition $3Li_2CO_3,Al_2O_3,3SiO_2$, Oliphant, Shire and Crowther[52] passed a beam of positive lithium ions through crossed electric and magnetic fields to collect 5×10^{-8} g. quantities of ^{6}Li and ^{7}Li on two small metal targets placed slightly apart. Collection of this quantity took 50 minutes for ^{6}Li and 5 minutes for ^{7}Li. The pure isotopes were fixed by admitting a little hydrogen chloride to form lithium chloride. Smythe and co-workers,[53] using a high intensity mass spectrometer with a Kunsman catalyst as source, achieved a higher ion current and collected several 10^{-6} g. samples of ^{6}Li and ^{7}Li. In their instrument the peaks for the two isotopes were separated in space by about 3 cm. Production-scale mass spectrographs, originally developed to enrich uranium-235, have recently been used for the separation of the lithium isotopes at ion currents up to several milliamperes.[55] With such currents lithium may be resolved into its isotopes at rates of the order of 0·1 g. per hour. Lithium chloride with a few per cent. of lithium metal is the charge material, and it is vaporized into the ionization chamber. The lithium metal is added to eliminate practical difficulties which are otherwise caused by dissociation of lithium chloride into $LiCl^+$, Li^+ and Cl^+. The large percentage mass difference between ^{6}Li and ^{7}Li permits the attainment of high isotopic purities.

Yatabe and Stedman,[56] following a detailed literature survey, considered methods of separating the lithium isotopes from the viewpoint of possible production in large quantities. The methods considered most suitable for successful separation of ^{6}Li and ^{7}Li were:-

1. distillation of lithium and its compounds;
2. liquid phase partition of lithium and its compounds;
3. chromatographic methods;
4. electro-migration methods;
5. combined chromatographic and electro-migration methods.

According to Bell,[57] separation of ^{6}Li and ^{7}Li by electrolysis would probably be less efficient than by other methods. Calculation of equilibrium data for the exchange reaction $^{6}LiH + {}^{7}Li \rightleftharpoons {}^{7}LiH + {}^{6}Li$ has led to an enrichment factor of 1·028 at 273°K., 1·025 at 298°K. and 1·008 at 600°K.[4] Lewis and MacDonald[58] changed the $^{7}Li/^{6}Li$ ratio from 11·6 to 5·1 by passing lithium amalgam through an 18 metre long column of lithium chloride in absolute alcohol or of lithium bromide in alcohol and dioxan. The lighter isotope accumulated at the foot of the column. Isotopic enrichment of lithium has also been reported by thermal diffusion in aqueous media,[59,60] by ion exchange,[61-64a] by electrolysis of aqueous solutions of lithium salts using a mercury cathode,[62-66] by electrolysis of fused lithium nitrate,[67] by electro-migration in fused chlorides[68] and by partial precipitation of lithium as carbonate[29a,69] and phosphate.[29a] Attempts to separate the isotopes by an electrogravitational method were unsuccessful.[70]

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SECTION IV

THE CHEMICAL PROPERTIES OF LITHIUM

By MRS. F. DICKINSON

Within the last two decades a good deal of interest has been centred on the chemistry of lithium since its production on a commercial scale is relatively recent, although the element has been known for more than a hundred years. Much of the early work on lithium has been repeated; further reactions, including those in liquid ammonia, have been studied; the application of the metal in the field of organic chemistry has been extended, and the alloying properties of lithium in examined some detail. This intensive study is reflected in the numerous additions made to the literature in the period now reviewed.

Lithium occupies the first position in Group I of the Periodic Table and, although in many ways a typical alkali metal, in some respects it closely resembles its neighbouring elements, magnesium and calcium in Group II. It is less reactive than the other alkali metals with water, oxygen and the halogens and more reactive with nitrogen, carbon and hydrogen. Its halides have a relatively high solubility in water while its carbonate and hydroxide are less soluble than those of sodium and potassium. The differences between lithium and the other alkali metals is partly explained by the fact that its ionic potential is greater and approaches the larger potentials of the alkaline earth ions.[1-3]

A freshly cut surface of lithium has a silvery appearance; on exposure to air the surface becomes dull and the corrosion products formed in the first five minutes have been shown by an electron diffraction study to be undoubtedly lithium oxide and lithium hydroxide. From the thermal data:-

$$Li + H_2O \rightarrow LiOH + 0{\cdot}5H_2 + 53{\cdot}2 \text{ kg.-cal.}$$
$$Li_2O + H_2O \rightarrow 2LiOH + 22{\cdot}3 \text{ kg.-cal.},$$

it is apparent that, with respect to water, lithium is in a higher energy state than lithium oxide and that lithium hydroxide is likely to be formed directly from the metal. On the other hand, the abundant supply of oxygen in the air may cause the oxide to be formed first. In a short exposure the carbon dioxide in the air has no effect on the metal, but on prolonged exposure, a soft, white deposit of lithium hydroxide and carbonate is formed.[4-7] The kinetics of the corrosive action of water vapour have also been studied. The black, glassy coating first formed persists for a time, dependent on the temperature and pressure of the water vapour, and then changes to a white material. Analysis of both the black and the white coating by an X-ray diffraction method shows that the only compound present is lithium hydroxide, but the black material is characterized by broad peaks and absence of some reflections, which suggests that a completely crystalline hydroxide is not formed during the early stages of the reaction. By observing the evolution of hydrogen as a function of time for several water vapour concentrations, the reaction, studied between 45° and 75°C., has been shown to proceed according to a logarithmic rate law: $W = k \log (1 + at)$, where W is the extent of reaction in time t and k and a are constants. The rate constant is independent of the water vapour pressure over a range of 22 to 55 mm. and the energy of activation for the reaction is found to be 6·2 to 5·5 kg.-cal./mol. depending on the pressure of the water vapour.[8] When lithium is stored in tins which are not quite air-tight, so that the air entering is largely freed from carbon dioxide and water vapour, a dense, brittle, reddish-brown material is formed which is believed to be lithium nitride.[2]

Lithium metal can be cut in air without danger of fire but its reactivity increases rapidly as the temperature approaches the melting point. Liquid lithium is readily ignited and once alight is difficult to extinguish because it reacts with most gases, with soda-ash and sand, with asbestos, concrete and asphalt, with carbon tetrachloride and in fact with almost all substances except metals, powdered graphite and zirconium silicate. The last two substances are those generally used to extinguish liquid lithium fires.[2,9,10] Although lithium salts give an intense carmine-red flame test, lithium itself burns, like magnesium, with a dazzling white flame.[11] The relative value of lithium as a rocket fuel has been considered and its ϕ value (*i.e.* the number of kg.-cal. per g. of a mixture of the fuel with the amount of oxygen required for complete combustion) compared with those of 33 possible gaseous and liquid organic compounds. These values vary from a minimum of 1·32 for acetaldehyde to a maximum of 3·21 for hydrogen, while the value for lithium is 4·72. Since, however, it is a solid up to 186°C., fuel tanks and lines containing lithium would have to be heated.[12]

A cost comparison has been made of high-energy rocket propellants including lithium, liquid ozone, liquid fluorine, chlorine trifluoride, fluorine monoxide, nitrogen tetroxide, liquid hydrogen, atomic hydrogen, liquid ammonia, hydrazine, liquid methane and beryllium. Liquid oxygen is likely to remain the cheapest oxidant but may meet competition from nitrogen tetroxide and liquid ozone.[13] Factors limiting the possible performance of rocket motors using chemical propellants have been discussed by Neat[14] and the mixture ratio, exhaust velocities for an expansion ratio of 50 and 250 *in vacuo*, combustion temperature and mean specific gravities of the mixtures are given for a number of known propellants, including a mixture of lithium and oxygen. Although a 1·2:1 mixture of oxygen to lithium has a higher bulk density than the liquefied gases cited, it appears doubtful that it will find extensive use because of the high molecular weight of the combustion products. Also, high exhaust velocities can be obtained only at the expense of high temperatures.

When lithium is burnt in excess of oxygen the monoxide, Li_2O, is formed and the dense white smoke produced is extremely irritating and obnoxious.[2] Despite the higher heat of vaporization and the higher ionic potential of lithium, the heat of formation of its oxide is considerably higher than that of any other alkali metal oxide. This is probably explained by the fact that the radii of the lithium and oxygen ions are small enough for them to approach closer than is possible, say, in the formation of cæsium oxide, and since the heat set free is inversely proportional to the square of the distance between the ions it is not surprising that the heat of formation of lithium oxide is relatively high.[1] The vapour pressures of lithium monoxide have been measured by an effusion method over the temperature range 1532° to 1669°K. and the equilibrium constant, K, calculated for the reaction:-

$$Li_2O_{(s)} = 2Li_{(g)} + 0{\cdot}5O_{2(g)}.$$

When $-\log K$ is plotted against $1/T$ the experimental points are mostly above the curve obtained by calculation from the heat of formation of the oxide from its gaseous elements and the free energy functions. In view of the somewhat high experimental results as well as the theoretical calculations of the stability of the oxides, Li_2O and LiO, it seems possible that the vapour of lithium monoxide may contain at least one of the gaseous oxides in concentrations comparable to those of the gaseous elements.[14] The peroxide is not formed in any quantity by the combustion of lithium, because it is thermally unstable and begins to lose its oxygen at 250° C. When oxygen is passed through liquid ammonia solutions of lithium, the initial blue colour of the solutions is destroyed and a white product, consisting chiefly of the monoxide with about 23% of the peroxide, is isolated on removal of the solvent.[16] Lithium does not dissolve readily at -78° C. in liquid ammonia but it may be oxidized at this temperature. If the metal is oxidized as it is added there is no initial blue colour, but instead a bright lemon yellow solution is obtained owing to the formation of a superoxide of lithium. If the temperature is allowed to rise to -33° C., the yellow colour fades and a white suspension forms; the colour changes cannot be reversed by cooling again to -78° C. Whether the metal is oxidized at -33° C. or -78° C. or whether the oxidation is effected in the presence or absence of excess metal, the white flaky product left on evaporation of the solvent is always the same, consisting of the monoxide with about 26% of the peroxide and about 5% of nitrite.[17] Lithium amalgam, 0·1%, reacts with oxygen when vigorously stirred at room temperature to give a 30% yield of lithium peroxide. This low yield may be due to a side-reaction by which the peroxide in the presence of excess lithium is converted into lithium oxide.[18]

When a lithium solution in ethyl alcohol is treated with hydrogen peroxide, lithium hydroperoxide monohydrate is formed. This compound, to which earlier workers[16,19] assigned the formula $Li_2O_2,H_2O_2,3H_2O$, has now been shown by analysis and *X*-ray powder diffraction studies to be LiO_2H,H_2O (Li_2O_2, $2H_2O$).[20] Solubility investigations of the ternary system, $LiOH-H_2O_2-H_2O$, at 10°, 0°, -10° and -21° C. reveal the solid phases, $Li_2O_2,H_2O_2,3H_2O$, Li_2O_2, $H_2O_2,2H_2O$ and $Li_2O_2,2H_2O$.[21] When the compounds, $Li_2O_2,H_2O_2,2H_2O$ and $Li_2O_2,2H_2O$ are heated to 150°-170° C., hydrogen peroxide and water are lost simultaneously and Li_2O_2 remains. This conversion gives a basis for ascribing the perhydrate composition, and not LiO_2H,H_2O, to the compounds.[22]

In the cold, lithium reacts slowly with water forming the strong base lithium hydroxide and hydrogen; at elevated temperatures the reaction is much more vigorous and enough heat may be generated to ignite the hydrogen.[2] Lithium hydroxide monohydrate, $LiOH,H_2O$, is produced when lithium, in the form of metal ribbon, is added to distilled water and the moist product, obtained by partial dehydration with phosphorus pentoxide at 20 mm. pressure and 25° C., is allowed to attain equilibrium with anhydrous lithium hydroxide.[20]

The intense blue-coloured solutions of the alkali and alkaline earth metals in liquid ammonia have been shown to contain the ordinary metal cations and ammoniated electrons[23] and it has long been supposed that similarly coloured solutions would be formed in water were it not that the metals react readily with the solvent. It has now been shown that when lithium is packed into a piece of glass tubing of small diameter and brought into contact with water, a blue line at the reacting surface is frequently visible.[24] The idea that the alkali metals may be physically soluble in water greatly affects the point of view adopted towards such processes as reduction by metal amalgams and the solution of the metals in acids.[25] The separation of hydrogen isotopes by displacement reactions of metals with water, acids or bases has been effected by several workers.[26-30] The metal is dissolved in the reagent of known deuterium content and the evolved hydrogen burned in a flame with a slight excess of oxygen. The proportion of the hydrogen isotopes in the water so formed is determined by density measurements. According to Johnston and Davies[30] the data are reproducible and confirm the applicability of the relationship, $d \ln [H] = \alpha\, d \ln [D]$ in which [H] and [D] are instantaneous values of the amounts of protium and deuterium in the liquid phase and α the "isotopic separation factor". For lithium and water at about 30°C. the above authors obtain a value for α of 1·84–1·86; for lithium and water and lithium and aqueous sulphuric acid Hughes, Ingold and Wilson[29] give values for α of 1·49 at about 40°C.

The heat of hydrolysis, corrected to infinite dilution and 25°C. for the reaction, $Li(s) + H_2O(l) = LiOH\ (\infty) + 0{\cdot}5H_2(g)$, is −53·10 ± 0·11 kg.-cal. per g.mol.[31]

Lithium combines with hydrogen at 680–700°C. at a rate such that 1·5 c.c. of the gas reacts with one sq. cm. of the metal per second.[32] Hydride formation begins before the metal is fused and the smooth reaction is probably due to the high solubility of the metal in the hydride.[33] The reaction has also been carried out by allowing hydrogen to react with freshly distilled lithium obtained by heating an intimate mixture of a lithium compound with a reducing metal, preferably aluminium, at a sufficiently high temperature to reduce the compound and distil the resulting metal.[34] In connexion with the synthesis of ammonia from metallic hydrides and nitrides, the rate of formation of lithium hydride has been studied between 400° and 525°C., and it has been found that the reaction proceeds comparatively slowly at 500° to 525°C., the metal absorbing about 118 times its volume of hydrogen in 30 minutes. Metallic promoters, particularly manganese and nickel in the proportions of 1:1, markedly increase the absorption of hydrogen by lithium. At higher temperatures and at pressures below atmospheric lithium sublimes freely.[35] Hurd and Moore[36] obtained a value of 44,000 ± 2,000 g.-cal. for the heat of the reaction:-

$$2LiH = 2Li + H_2$$

by plotting their experimental values of log p against $1/T$ over the temperature range of 509–653°C. Guntz and Benoit,[37] by calorimetric measurements, found a value of 43,600 g.-cal. The heat of formation of lithium hydride has been calculated from the difference between the heats of reaction of the hydride and the metal with water, measured by carrying out the reaction in a specially designed bomb enclosed in an adiabatic calorimeter jacket. The value obtained for LiH is −21·34 ± 0·09 kg.-cal. per mole.[38,39] A later publication gives −21·34 ± 0·15 kg.-cal. per mole.[31] The stability of the alkali and alkaline earth hydrides decreases in the order Li, Ca, Sr, Ba, Na, K and this is another example of the close relationship of lithium with the alkaline earth metals. The melting point of lithium hydride is 680°, and at 640° the vapour pressure does not exceed 70 mm. of mercury.[33] It is worthy of note that the first instance of hydrogen appearing as a negatively charged ion was established when lithium hydride was electrolyzed; the hydride is regarded as a salt and the relationship of hydrogen to the halogen family is further demonstrated by the similarity of the atomic arrangement in LiH and NaCl.[1,38] From a calculation of the energy of interaction of lithium ions with hydrogen, using the Heitler–London method, it has been concluded that a stable system cannot be formed.[40] Perturbation theory has been applied to calculate the effect of the hydrogen atom at the bonding distance from lithium. The H_{mn} terms^{a} for the systems, H_{1s1s} and H_{1s2s} and H_{1s2p} are $-3{\cdot}87 \times 10^{-3}$, $-5{\cdot}69 \times 10^{-4}$ and $-1{\cdot}50 \times 10^{-3}$ respectively (a, 1 atomic unit = 27·205 eV).[41]

The binary systems of lithium with mercury have been investigated and heating and cooling curves prepared for sixty-seven alloys. The lithium–mercury system, as constructed from these data, comprises: $LiHg_3$ (0·6–18% Li), $LiHg_2$ (18–29% Li), solid solutions of LiHg (29–70% Li), Li_2Hg (70–72%

Li), Li_3Hg (72-91% Li), Li_6Hg (91-92% Li), solid solutions of Li (92-100% Li). There is a eutectic point at -42°C., corresponding to 0·6% Li, and another at 160°C. with 92% Li; the compounds Li_3Hg, m.p. 375°C., and LiHg, m.p. 590°C., fuse without decomposition, and the upper limits of existence for the other compounds are 164°C. for Li_6Hg, 375°C. for Li_2Hg, 340°C. for $LiHg_2$ and 235°C. for $LiHg_3$.[42] X-Ray analysis gives results in agreement with the thermo-analytical data.[43] Lithium amalgam reacts with carbon dioxide to form the oxalate, and the presence of small amounts of water or oxygen results in the formation of considerable amounts of carbonate. It has been shown by thermodynamic calculations that lithium amalgam can reduce carbon dioxide to carbon monoxide.[44-46] According to Henglein and Sontheimer,[45] yields of 0·1 and 4·5% of lithium oxalate are obtained at 20°C. and 250°C. respectively and small amounts of other complex substances as well as carbonate are formed. The yield of oxalate from metal amalgams is related to the half-wave potential of the amalgams. The presence of carbonate is explained by the following equations:-

$$2Li + CO_2 = Li_2O + CO; \quad Li_2O + CO_2 = Li_2CO_3.$$

Hohn, Fitzer and Nedwed[47] detected no carbon monoxide in the reaction products and no by-products when moisture and oxygen were rigidly excluded. They obtained 1·38 g. *i.e.* a 62·2% yield of lithium oxalate in 83 minutes from a 0·032% lithium amalgam at room temperature.

At high temperatures lithium combines readily with the halogens to form the corresponding halides. The energies of combination of the gaseous metal ions with gaseous halogen ions to form solid halides have been calculated from the best available thermochemical and spectroscopic data and it has been found that for the larger alkali metal and halogen ions the values are all about 165 kg.-cal. For the smaller ions the energy of combination increases, becoming 235 kg.-cal. for lithium fluoride. This probably accounts for the fact that the compounds formed from elements of low atomic number are highly stable compared with what would be expected from such electrochemical criteria as the 'replacement series'.[48] The 'standard state' heat of formation per g. equivalent of crystalline lithium chloride, *i.e.* the heat of formation of the compound from its elements in the standard state divided by the valency, plotted against the logarithm of the product of the atomic numbers of the elements, falls on the straight line obtained for the chlorides of the other alkali metals. Since a linear plot is also obtained for the chlorides of the alkaline earth metals, for those of boron, aluminium, scandium, yttrium and lanthanum and for the chlorides of carbon, silicon, titanium and zirconium, both along the groups and periods, an unknown $-H$ value may be safely predicted by interpolation or extrapolation, provided that the elements are in the standard state.[49]

The chemiluminescence exhibited when iodine reacts with lithium in the vapour phase has been examined spectroscopically. The first lines of the principal series of lithium are present and faint; apparently continuous bands are also seen, but the lines are more diffuse than would be expected from the pressure, which never exceeded 15 mm. The available energy data are not sufficient to explain these results.[50]

Chemical reactions between lithium and water, acids and caustic alkalies have been investigated, the reaction velocity being plotted against log $[H^+]$, taking that with water as 100. Graphs are given for hydrochloric, sulphuric, nitric, acetic and boric acids and for caustic soda solutions, and it is concluded that the observed effects are the combined result of the reactions: $2H^+ + Li \rightarrow H_2 + 2Li^+$ and $2H_2O + 2Li \rightrightarrows H_2 + 2OH^-$. The reaction which continues when the $[H^+]$ is below the concentration in dilute acid is that producing hydrogen gas directly from the water molecule.[51]

Sulphur vapour reacts with heated lithium to give a yellowish amorphous powder of lithium sulphide,[52] Li_2S, but according to later workers[53,54] the colouration is due to oxidation on exposure to air. The reaction between the elements, when either is molten, is very violent; even under an organic liquid serious decomposition of the liquid occurs and the product is contaminated with carbon and metallic carbide. The following example is given: lithium, 1 g., is melted under 150 ml. of boiling naphthalene and sulphur is added through a reflux condenser in 0·5 g. portions. No reaction occurs until 0·5 g.-atom has been added when a reaction starts with explosive violence. Further quantities of sulphur do not appear to react. The material is filtered from the liquid naphthalene, thoroughly washed with boiling toluene and strongly heated in a vacuum to expel residual solvent. On treatment with water, hydrogen and hydrocarbons are evolved from free metal and carbides and free carbon is deposited. Analysis shows that the main product of the reaction is lithium monosulphide and that the polysulphide is present only in minute amounts.[55] Sulphur reacts very vigorously with solutions of lithium in liquid ammonia at -33°C., producing initially a slightly soluble, white, amorphous precipitate of the monosulphide, Li_2S. Further reaction with sulphur leads to the formation of a light yellow or orange disulphide, and this in turn reacts with more sulphur giving a tetrasulphide which is readily soluble in liquid ammonia forming an intense orange-yellow solution. The reactions may be represented thus: $2Li + S \rightarrow Li_2S$; $Li_2S + S \rightarrow Li_2S_2$; $Li_2S_2 + 2S \rightarrow Li_2S_4$; $Li_2S_4 + (n-4)\,S \rightarrow Li_2S_n$. After removal of the solvent, the polysulphide is separated from unchanged sulphur by the action of water vapour. The sulphides containing four or more atoms of sulphur retain several molecular proportions of ammonia when dried *in vacuo* at 20°C. but the tetrasulphide loses nearly all the ammonia when heated at 140°C. under reduced pressure. The monosulphide has been isolated as a white powder which rapidly becomes coloured on exposure to air.[53,54] The heat of formation of Li_2S is 57·5 kg.-cal./ mole equiv. according to Osborg[1] but more recently Juza and Uphoff have given a value of 106·5 kg.-cal. per g.-mol. for the reaction: $2Li_s + S_{rh} = Li_2S_s$.[56]

Selenium, like sulphur, reacts very readily with lithium dissolved in liquid ammonia at -33°C. Initially a white, sparingly soluble and apparently amorphous precipitate of the monoselenide, Li_2Se, is formed. The reaction occurs within five to twenty minutes, the time varying inversely as the concentration of the lithium in solution. With excess of selenium the soluble diselenide, Li_2Se_2, is first formed, further reaction producing very soluble polyselenides the formation of which is accompanied by an intense colour change. Usually it takes one to two days to establish equilibrium between the polyselenide solutions and selenium, and the average composition of the selenide then appears to be $Li_2Se_{5\cdot4}$. It is believed that this substance is a mixture of Li_2Se_4 and a higher polyselenide, perhaps Li_2Se_6. The monoselenide is isolated as a white ammine and when heated at 150°C. in a vacuum it changes to a reddish-brown ammonia-free salt. The selenides are readily oxidized in moist air with the separation of selenium.[53,54,57]

Lithium and tellurium react together in liquid ammonia solution forming a white product, Li_2Te, which rapidly becomes coloured on exposure to air.[54]

When hydrogen sulphide is passed into ether to which lithium metal has been added, hydrogen is liberated at the surface of the metal and a white precipitate collects at the bottom of the container; the reaction is complete in about twenty-four hours and the product, which is free from polysulphides, has been shown to be lithium hydrogen sulphide, LiHS. This compound readily combines with alcohol forming the alcoholate, $2LiHS,C_2H_5OH$.[58] When the alcoholate is heated very rapidly to 360°C. in an evacuated vessel, a faintly yellowish-brown product containing approximately 55·6% of the monosulphide is obtained; the remainder is lithium ethoxide. On passing hydrogen, with about 10% of hydrogen sulphide, over the material at 120°C., the ethoxide is reconverted to lithium hydrosulphide and alcohol distils over. When the mass is heated to 360° in the presence of phosphoric oxide and solid potassium hydroxide, nearly pure lithium monosulphide is produced together with a very small quantity of polysulphide. When an alcoholic solution of lithium hydrosulphide is boiled with excess of sulphur in a current of dry hydrogen, hydrogen sulphide is rapidly evolved and the solution becomes dark red. The only polysulphide obtained is the disulphide, $Li_2S_2C_2H_5OH$.[59]

Lithium reacts with alcohol to form lithium ethoxide as a suspension. On treatment with hydrogen sulphide, the ethoxide is converted into lithium hydrosulphide, LiHS, and on removal of excess of hydrogen sulphide, by boiling in a stream of nitrogen, and addition of an equivalent amount of lithium ethoxide to the colourless solution, lithium monosulphide, Li_2S, is formed. The action of sulphur on aqueous, aqueous-alcoholic, and anhydrous alcoholic solutions of lithium monosulphide give polysulphide solutions from which crystalline products cannot be isolated. Alcoholic solutions of lithium hydrosulphide, with various proportions of sulphur, yield lithium tetrasulphide, Li_2S_4, and on crystallization at room temperature, the composition of the crystals corresponds to the formula, $Li_2S_4,2C_2H_5OH$. With less sulphur, mixtures of tetrasulphide and unchanged hydrosulphide are obtained. Higher polysulphides may be formed but cannot be isolated by crystallization. At the boiling point of the solutions only an alcoholated disulphide, Li_2S_2,C_2H_5OH, can be separated. The disulphide is far more stable than the tetrasulphide.[55] Lithium hydrogen sulphide is also formed by the action of hydrogen sulphide on lithium amylate. It is sensitive to air and decomposes at about 50°C. The enthalpy of formation of lithium hydrosulphide from its elements is −60·0 kg.-cal. per g.-mol.[60]

It is believed that the alkali-metal hyposulphites have not been successfully prepared by direct action between an alkali metal and sulphur dioxide. When, however, the alkali metal is in the form of an addition product with certain ethers, the hyposulphites can be conveniently prepared in good yield by treating the reaction products with sulphur dioxide. In the case of lithium, the metal–ether addition product is best prepared by using the metal in the solid state. At temperatures above the melting point of lithium there is some tendency for the metal to split the ether. The ether may be ethylene glycol dimethyl ether but other ethers of polyhydric alcohols may be used (see also Sect. XXV)[61]

At high temperatures lithium reacts with gaseous ammonia giving lithium amide, $LiNH_2$, and hydrogen. The same products are obtained when lithium solutions in liquid ammonia are allowed to stand in the presence of metal catalysts. The reaction takes about eight days when the solution, in a sealed tube containing platinum gauze, is exposed to light.[62-64] Benoit attributes the increase in rate of reaction which he observed to the presence of impurities, probably potassium, in the lithium metal.[65] Iron wire has also been used as a catalyst.[66] The amide is a white crystalline substance and its heat of formation is 42 kg.-cal./mol.[64]

The reaction of lithium with ammonia to give the amide is slower than the corresponding reaction of cæsium, and the same difference is observed in the reaction with methylamine; the heavier is the alkali metal the quicker is the reaction. The blue solution of lithium in methylamine, when heated in a sealed vessel at 50–60°C., decomposes to a white powder which is almost insoluble in methylamine: $Li + CH_3NH_2 \rightarrow CH_3NHLi + \frac{1}{2}H_2$. The methyl-amide decomposes still further on heating to give the imide: $2CH_3NHLi \rightarrow CH_3NLi_2 + CH_3NH_2$; and cautious thermal decomposition in a high vacuum gives a mixture of the imide and cyanide.[67]

At room temperature, lithium reacts very slowly with nitrogen forming lithium nitride, Li_3N; the speed of the reaction increases greatly as the temperature approaches the melting point of the metal.[2] In connexion with the formation of metallic hydrides and nitrides and their significance in the synthesis of ammonia, the activation energy of adsorption of nitrogen on lithium has been evaluated at 47 kg.-cal. per mole. An investigation of the rate of reaction between nitrogen and lithium has been carried out at 400–500°C. and the velocity constants have been determined between these temperatures. The metal absorbs about 300 times its own volume of the gas, in conformity with the formula Li_3N. The nitride is a dark grey solid which absorbs moisture rapidly from the air, liberating ammonia. Metallic promoters have little appreciable effect on the absorption of nitrogen by lithium, but of those tested cæsium is the best.[35] A small quantity of nitride, but no azide, is formed when nitrogen activated by an electric discharge reacts with lithium; in this respect lithium differs from the other alkali metals which give azides.[68] The electrolysis of an alcoholic solution of lithium chloride in a cell placed in a hermetically sealed chamber filled with nitrogen at a pressure of 1000 atm. yields lithium nitride as an intermediate product in the preparation of ammonia: $Li_3N + 3C_2H_5OH \rightarrow 3LiOC_2H_5 + NH_3$.[69] Nitrogen is removed from combustible gases by bringing the mixtures into contact with a lithium amalgam to form lithium nitride, Li_3N. The lithium nitride-mercury mixture from the scrubbing vessel is treated with water to produce ammonia and lithium hydroxide from which lithium may be recovered by electrolysis in the presence of mercury or a fusible alloy, preferably used as a liquid cathode. The process is particularly suitable for removal of nitrogen from natural gas.[70]

Phosphorus combines with lithium at 680°C. to give a reddish-brown mass of lithium phosphide, Li_3P. A brownish-black compound, Li_3As, is formed when lithium and arsenic are heated together at 800°C. Juza and Schulz[71] state that the reactions between lithium and phosphorus, and lithium and arsenic, in an argon atmosphere, are so violent that the phosphorus and arsenic should be added in small portions at a time. The arsenide is also obtained as a fine brown powder by adding a solution of lithium in liquid ammonia to a suspension of powdered arsenic in the same liquid, and under similar conditions antimony yields the blue-grey antimonide, Li_3Sb. The reaction between red phosphorus and lithium in liquid ammonia does not go to completion.[72] Phosphine reacts readily with lithium in liquid ammonia solution with the formation of lithium dihydrogen phosphide and the liberation of hydrogen. At 0°C. the tetra-ammoniate of this compound may be isolated, but on raising the temperature it is thermally decomposed to the di- and mono-ammoniate. The last molecule of ammonia cannot be removed without the loss of 0·5 mole of phosphine per mole of phosphide, and the final product obtained by heating to 50°C. is dilithium hydrogen phosphide, Li_2PH.[73] A similar reaction occurs when arsine in passed into a liquid ammonia solution of lithium. At -70°C. the metal solution is rapidly decolorized, hydrogen is evolved and the ammoniate, $LiAsH_2,4NH_3$, is formed; on warming up to 0°C. in a vacuum, ammonia is given off leaving the diammoniate which may be further decomposed by heating to 70°C. to dilithium hydrogen arsenide, Li_2AsH, and finally to lithium arsenide, Li_2As. No further change occurs on heating to 450°C.[74]

Lithium reacts rapidly but quietly with liquid dinitrogen tetroxide yielding the insoluble nitrate, free from nitrite, and nitric oxide.[75] A radical-like salt is formed when lithium is added to sodium nitrite in liquid ammonia; the compound, $LiNaNO_2$, which is regarded as a salt of the unknown 'hydronitrous' acid, H_2NO_2, is very reactive towards moisture, air and carbon dioxide and decomposes violently at 100–130° C.[76]

Boron does not react directly with lithium. Boric acid in alcoholic solution when added to lithium in absolute alcohol gives a white crystalline precipitate of lithium borate, Li_2O, B_2O_3.[77] Metallic borohydrides are excellent reducing agents, providing efficient sources of hydrogen, and may be used for production of diborane and related boranes. The following typical reactions occur: $4Li + 2H_2 + BF_3 = LiBH_4 + 3LiF$; $4Li + 2H_2 + B(OCH_3)_3 = LiBH_4 + 3LiOCH_3$; $6Li + 3H_2 + 2BF_3 = B_2H_6 + 6LiF$.[78]

Elemental boron in a high-density crystalline form is prepared by a continuous process in which boron trifluoride in the gaseous form is caused to react with a gaseous dispersion of an alkali metal. The example cited is: $BF_3 + 3Na \rightarrow B + 3NaF$, but other alkali metals may be used.[79] According to Moissan,[80] deep blue, small, lustrous crystals of lithium silicide, Li_6Si_2, are obtained when lithium and silicon are heated at 400–500° C. in a vacuum; the excess of lithium metal is removed by distillation at a temperature not exceeding 600° C. because above that temperature the silicide decomposes giving off lithium vapour and leaving amorphous silicon as the residue. More recently Osborg[81,82] has shown that it is possible to prepare a number of 'alloys' of lithium and silicon by heating the elements together at temperatures above 600° C. in an evacuated container. The 'alloys' are solid, hard, uniform masses of metallic appearance having the compositions and properties given in Table I.

TABLE I. - PROPERTIES OF 'ALLOYS' OF LITHIUM WITH SILICON

Composition % Li	Composition % Si	Density	Freezing Range °C.	Author
60	40	About 1·0	500–550	Osborg[81]
50	50	1·17	About 625	Osborg[81]
40	60	1·4	680–700	Osborg[81]
25	75	1·72	700–750	Osborg[81]
Li_6Si_2 42·3	57·5	1·12	Decomposes above 500	Moissan[80]

Klemm and Struck have found that when lithium–silicon mixtures in the ratios of Li : Si <2 : 1 or >4 : 1 are heated under argon in nickel crucibles to temperatures not exceeding 650°C., part of the silicon or lithium is unaffected. A 2 : 1 mixture, tempered at about 530°C., is a dark blue-violet substance; a 4 : 1 mixture tempered at about 630°C., is a silver-grey substance. Chemical analyses and *X*-ray examinations agree with the formulæ Li_2Si for the blue and Li_4Si for the grey compound. Under other conditions, products of indeterminate colour, or two separable phases, are obtained. The existence of Moissan's compound, Li_3Si, has not been confirmed.[83]

The solubility of lithium in silicon has been determined by measuring the change in resistivity upon saturation at a series of temperatures between 450° and 1000°C.; the results are given in the form of a solubility curve.[84] Reiss and Fuller[85] from theoretical considerations of ionization and solubility in semi-conductors, constructed a solubility curve which agreed with experimental data with the exception of the point at 500°C. which was considered to be in error. Pell[86] has also measured the solubility of lithium in silicon between 600° and 1400°C., and found that at higher temperatures it is not possible to quench rapidly enough to prevent serious precipitation, as revealed by comparing electrical measurements of lithium remaining in solution after cooling with chemical measurements of total lithium content. Total lithium content has, therefore, been determined by flame analysis and the resulting solubility agrees with previous electrical measurements[87] at 600°C. but departs markedly from them at higher temperatures and in general follows the curve predicted from thermodynamic principles.[88] Reiss and Fuller[89] have since analyzed the specimens used in their electrical measurements and agree now with the results obtained by Pell.

Lithium combines with carbon at a red heat to give lithium carbide; with sugar charcoal reaction occurs with incandescence; with graphite and diamond there is no incandescence: 2C (diamond) + 2Li (solid) → Li_2C_2 (solid) + 11·3 g.-cal. In preparing the carbide it is necessary to use a double tube, one of porcelain inside a glass tube, because lithium vapour attacks the porcelain and may cause it to fracture; and the reaction should be carried out in a vacuum for at a red heat lithium absorbs most gases. The temperature should be raised slowly as the lithium carbide formed will otherwise decompose very rapidly to lithium and carbon; prolonged heating has the same effect. Lithium carbide is also formed when carbon is heated with substances which dissociate to give lithium; lithium hydride and lithium nitride for example will thus give lithium carbide, and in the latter case lithium cyanide is also produced. Carbon cannot be used as an electrode in the electrolysis of fused lithium chloride because the lithium carbide formed at the temperature of electrolysis diffuses into the chloride mass and is there decomposed giving carbon which remains in suspension in the liquid.

Compounds containing carbon are also decomposed when heated with lithium; carbon monoxide forms lithium carbide when passed over lithium at red heat. If a stream of carbon dioxide is passed over heated lithium, at a rate slow enough to prevent the temperature rising above red heat, lithium carbide is obtained, but if the temperature is allowed to rise higher only a small amount of carbide is formed. If lithium is gently warmed in pure ethylene the metal is at first covered with a white incrustation; if the temperature is then raised to about 700°C. the coating melts and the lithium becomes incandescent because of the heat evolved in the absorption of ethylene. A molten greyish-white product is obtained with no deposition of carbon, and analysis shows it to have the composition $C_2H_4Li_6$. The product is probably a mixture of lithium carbide and lithium hydride, for on treatment with water acetylene, hydrogen and lithium hydroxide are formed: $C_2H_4 + 6Li \rightarrow Li_2C_2 + 4LiH$; $Li_2C_2 + 4LiH + 6H_2O \rightarrow C_2H_2 + 4H_2 + 6LiOH$. Metallic lithium is an active promoter in ethylene polymerization. Mixtures of alkali metals and oxides of Group 6A of the periodic table (chromium, molybdenum, tungsten or uranium) are used as catalysts for the polymerization of ethylene, propylene or their mixtures to produce solid polymers of high molecular weight. The reaction is carried out at 130°–260° and 1000 lb. per sq.in. pressure in a liquid medium. Benzene, toluene or xylenes are preferred media for the polymerization of ethylene, and *cyclo*hexane, decalin or *iso*-octane for the polymerization of propane. The alkali metals alone are not catalysts; it might be assumed that they function by reacting with catalyst poisons which might be present in small proportions of the order of a few p.p.m. When no alkali metal is present, a subhexavalent Group 6A metal oxide is required as catalyst but with an alkali metal present the catalyst can be a Group 6A solid oxide in the form of a trioxide. The proportion of alkali metal can be varied from 0·001 to about 2 parts by weight per part by weight of the metal oxide catalyst. Many different types of supports for the catalyst, including γ-alumina, can be used when alkali metals are present. The promoting activity of the metal increases with increasing atomic weight.[90] When lithium is warmed slowly in an iron vessel in a stream of acetylene an abundant deposit of carbon is obtained with the formation of some acetylide and hydride. If the metal is heated under reduced pressure and acetylene is passed briskly over the lithium, heat is evolved and lithium carbide and hydride are obtained: $C_2H_2 + 4Li \rightarrow Li_2C_2 + 2LiH$. In this case there is only a slight deposit of carbon.[91-93] It has been suggested that fused salts containing metal ions should catalyze reactions that are normally brought about by the corresponding metals in the free state and lithium chloride, like lithium, causes the pyrogenic decomposition of acetylene at 600°C.[94] Liquid ammonia solutions of lithium react with acetylene to give lithium acetylide, $LiHC_2$, which is stable and free from carbide as long as it remains in solution; attempts to isolate it, however, by removal of the solvent result in spontaneous decomposition to the carbide and the product is a mixture of 82% of lithium carbide and 17·6% of the acetylide.[95] Lithium reacts with trifluoromethyl hypofluorite, CF_3OF, to give carbonyl fluoride and lithium fluoride: $2Li + CF_3OF = 2LiF + COF_2$. The reaction is slow at room temperature; over a period of hours the original lustrous metal surface is completely tarnished and carbonyl fluoride formed, but much of the hypofluorite remains unchanged. When the glass reaction vessel is heated to a temperature near the melting point of lithium, a strong reaction occurs with the liberation of enough energy to melt the glass. This reaction is accompanied by the intense carmine-red light characteristic of lithium.[96]

Gaseous hydrogen cyanide passed over lithium at 570°C. in the absence of air yields a grey product which when freed from excess of metal contains 35·8% of lithium cyanide and 43·2% of lithium cyanamide. A 20% solution of hydrogen cyanide in anhydrous ether reacts immediately with lithium forming a white precipitate which after washing with ether and drying in vacuo at 100°C. is found to contain 84% of lithium cyanide. A similar reaction occurs when a 50% solution of hydrogen cyanide in benzene is used and if the reaction is carried out quickly the product contains 99% of lithium cyanide. To obtain pure lithium cyanide it is essential to use rigorously dried materials.[97,98] At temperatures not higher than 300°C., cyanogen forms lithium cyanide and paracyanogen, $(CN)_6$, when the gas is led into an iron vessel containing lithium, but above this temperature appreciable quantities of lithium cyanamide are produced: for example, when a temperature of 400°C. was reached over a period of six hours the product contained 20% of lithium cyanide and 29·2% of lithium cyanamide, the remainder being paracyanogen. The suggested mechanisms for the reactions are: $2Li + (CN)_2 \rightarrow 2LiCN$; $2Li + (CN)_2 \rightarrow Li_2NCN + C$; or $2LiCN \rightarrow Li_2NCN + C$.[97] The formation of lithium cyanamide in various reactions, however, indicates that it is a transformation product of lithium cyanide.[99]

In its behaviour towards constructional metals and alloys lithium is found to be more difficult to contain than sodium (see Sect. XXV). Austenitic steels, nickel-base alloys, manganese and cobalt-base alloys, and copper and copper alloys all show a poor resistance to molten lithium. Vanadium, beryllium and chromium are severely attacked. Mild steel may be used to store or melt lithium. 'Armco-iron' is efficient up to 600°C., stainless steel to 500°C., and low-carbon steels to 700°C., while columbium, tantalum and molybdenum resist attack up to 1000°C. Zirconium and titanium show a fair resistance to attack.[2,100-102] The leaching of nickel from the surface of 304 stainless steel by the action of molten lithium at 1000°C. is described by Brasunas[103] and photomicrographs are given. Bar graphs giving temperatures below which systems may be operated with lithium for 1000 hr. with less than 0·005 in. attack on iron, low-alloy steel, ferritic stainless steel, austenitic stainless steel, nickel, 'inconel,' cobalt, 'stellite,' copper, copper-base alloys, refractory metals (molybdenum, niobium, tantalum, zirconium, titanium, tungsten and vanadium) and precious metals, silver, gold and platinum are given both for static and dynamic systems. Lithium nitride, Li_3N, is the most harmful contaminant when working with lithium. No satisfactory material has been found to handle lithium in dynamic systems above 1200° F. Below 1000° F., the stainless steels give good resistance.[104, 105]

The heats of reduction of twenty five oxides of metals and metalloids by lithium and by thirteen other elements have been calculated in order to compare them with the normal electromotive potentials of the elements: there appears to be a parallelism between the heats of reduction and the potentials indicating that the thermal reduction processes are ionic reactions.[106] Oxides or oxygen-containing compounds with uranium in the acid radical are reduced by fused lithium or alloys of lithium with sodium or potassium, with or without carbon or magnesium. Gases such as oxygen, nitrogen, hydrogen or carbon dioxide must not be present. In the following reaction: $U_3O_8 + 16Li = 3U + 8Li_2O$, 813 g. of the oxide and 132 g. of lithium, *i.e.* 25 g. excess of lithium, are heated together in argon. The initial temperature is 390°C., the maximum temperature, 985°C. Lithium oxide and excess of lithium are leached from the reaction products with water, hydrochloric acid is added to the solution to bring the pH down to about 6 and the resulting lithium chloride solution is evaporated to dryness, mixed with potassium chloride, fused and electrolyzed to produce lithium metal which may be used again. Alloys of uranium may be produced by reducing a uranium compound mixed with a compound such as the oxide of the desired alloying constituent. Instead of lithium, alloys such as lithium-sodium, lithium-potassium or lithium-sodium-potassium may be used.[107]

Titanium oxide is reduced to titanium by heating with lithium: 80 g. of lithium (25 g. excess) in the form of three slabs 2·5 × 2 × 0·75 in. is placed in a steel pan and loosely surrounded on all sides with 160 g. of finely powdered titanium oxide, TiO_2. The pan is placed in a low-carbon steel retort, the head is bolted to the end of the retort, the air evacuated and argon introduced. The charge is heated and the initial reaction sets in at 200–400°C., depending upon the grade and quantity of the charge. The reaction is indicated by a flash of light and a rapid temperature increase to a maximum of 700–900°C. The temperature then falls to about 600°C. and is brought up to 675°C. and maintained there for about 0·5 hr. The retort and charge are allowed to cool to room temperature, the reaction products are removed from the retort in the container and placed in water. After leaching out lithium monoxide, Li_2O, and excess lithium, the finely divided titanium metal is removed by filtration, thoroughly washed and dried. The solution of lithium hydroxide is treated with hydrochloric acid, evaporated to dryness, mixed with potassium chloride, fused and electrolyzed to recover lithium metal for recycling: $TiO_2 + 4Li = Ti + 2Li_2O$; $Li_2O + H_2O = 2LiOH$; $2Li + 2H_2O = 2LiOH + H_2$; $LiOH + HCl = LiCl + H_2O$. When the charge of lithium metal is four times as large, the maximum reaction temperature exceeds 1400° C. The following reactions are carried out in a similar manner: lithium titanate, 110 g., lithium, 70 g., excess lithium, 42 g., initial temperature of reaction, 475°C., maximum temperature, 790° C.: $Li_2TiO_3 + 4Li = Ti + 3Li_2O$. Vanadium pentoxide, 67 g., lithium, 32 g., excess lithium, 6 g., initial temperature of reaction 394° C., maximum temperature, 768° C.; $V_2O_5 + 10Li = 2V + 5Li_2O$. Niobium pentoxide (87·8% Nb_2O_5), 20 g., lithium, 10 g., excess lithium, 5 g., initial temperature of reaction is 320° C., maximum temperature, 490° C., $Nb_2O_5 + 10Li = 2Nb + 5Li_2O$. Tantalum pentoxide, 72 g., lithium, 7 g., initial temperature of reaction 410° C., maximum temperature 595°C. $Ta_2O_5 + 10Li = 2Ta + 5Li_2O$. The source of tantalum pentoxide is an ore containing a high percentage of the pentoxide. Chromium oxide, 200 g., lithium, 70 g., excess lithium 16 g., initial temperature of reaction about 180°C., maximum, 965°C. $Cr_2O_3 + 6Li = 2Cr + 3Li_2O$. Molybdenum oxide, 194 g., lithium, 70 g., excess lithium, 14 g., initial temperature of reaction 180°C., maximum temperature >1400°C. $MoO_3 + 6Li = Mo + 3Li_2O$. Tungsten oxide, 153 g., lithium, 37 g., excess lithium, 10 g., initial temperature of reaction 200°C., maximum 1030°C. $WO_3 + 6Li = W + 3Li_2O$. Manganese telluride, 170 g., lithium, 20 g., excess lithium, 7 g., initial temperature of reaction 230°C., maximum temperature, 660°C., $MnTe + 2Li = M + Li_2Te$. Iron sulphide, 240 g., lithium, 10 g., excess lithium, 15 g., initial temperature of reaction 260°C., maximum temperature 945°C. $FeS + 2Li = Fe + Li_2S$. The metals, magnesium, calcium, barium and cerium cannot be obtained in the pure state by the above method but are produced as lithium alloys.[108]

It is more difficult to displace lithium from its salts by reaction with other metals than it is to effect a similar reaction with salts of the other alkali metals, and this is believed to be due to the higher heats of formation of lithium salts and the higher boiling point of lithium; thus, the fluoride and chloride of lithium can be heated with iron in a vacuum at 1000°C. without any reaction occurring[109] (see page 6). Cerium trifluoride is reduced by lithium to cerium: $CeF_3 + 3Li \rightarrow Ce + 3LiF$. The heat of reaction is 27 kg.-cal./g.-mol. of CeF_3 at 400°C. In order to obtain the best possible separation between cerium and flux, the reaction products and the remainder of the reactants should be melted during the course of the reaction. There is small likelihood of the reactants reaching a temperature at which they will all be molten solely as a result of the heat of reaction, but the deficiency can be met either by heating the reactor externally after the reaction is complete, or by boosting the reaction with an additional simultaneous reaction. In the first case contact between the molten cerium metal and the walls of the reactor will be prolonged and the risk of contamination of the cerium thereby increased. In the second case a suitable booster reaction is that between lithium and iodine which liberates 66·43 kg.-cal./g.-mol. of lithium iodide. The reactor is constructed of mild steel tubing, 1·75 in. internal diameter by 10 S.W.G. wall, the bottom, flange and lid being made from 0·25 in. mild steel plate. A gasket of 16 S.W.G. copper wire is used between the flange and lid and is satisfactory although not gas-tight. Molybdenum has been found to be the best lining material and the lining consists of a molybdenum can 4·5 in. high by 1·5 in. diameter. The reactants are pressed into pellets only slightly smaller in diameter than the inside of the can, and loaded into the can which is then placed on a bed of calcium fluoride in the reactor. A disc of molybdenum is placed on top of the can and more loose calcium fluoride added for heat insulation. There is a small space all around the outside of the can permitting free radiation from the inner wall of the reactor. If iodine is absent from the charge the reactor is evacuated and filled three times with argon; if iodine is used the above practice is abandoned because the vapour pressure of iodine is too high at room temperature.

The loaded reactor is sealed and placed in a 'Kanthal'-wound pot furnace heated to at least 1300°C. After about 15 min. the temperature of the outside wall of the reactor is about 1100°C. and this temperature is maintained for a further 30 min. by adjusting the furnace temperature. The reactor is removed from the furnace, allowed to cool, and the can is taken out of the reactor and opened up down its length. Cerium is at the bottom, the flux on top, cleanly separated from it, and excess lithium on top of this. A certain amount of cerium is always present on the inside walls of the molybdenum can throughout its whole height. Consistently high yields of cerium are obtained by this procedure with efficiencies up to 82·5%. The lithium–cerium fluoride reaction is apparently initiated at about 600°C., the lithium–iodine reaction at 200°C., and although the latter apparently contributes no useful heat to the system it appears to reduce the melting point and increase the fluidity of the slag. A typical charge for the reactor is: 110 g. cerium trifluoride, 20 g. iodine, 14·1 g. lithium (11·7 g. to react with cerium fluoride, 1.1 g. to react with iodine and 10% excess). This is compacted into five or six pellets each containing the same proportion of reactants, packed in layers to give the closest approximation to intimate mixing. The molybdenum can adheres so strongly to the cerium button that it has to be filed off it. If, however, a $\frac{1}{32}$-inch layer of cerium immediately below the can is also removed, molybdenum contamination is negligible. Small quantities of occluded flux can be easily removed by remelting in ceria crucibles in a vacuum better than 0·0001 mm. Hg. Metal of 99·92 to 99·93% purity is consistently made.

A similar reaction has been carried out by using cerium trichloride in place of the trifluoride but the reaction is not nearly so successful because although cerium is produced it does not coalesce but remains finely dispersed throughout the reaction cake. Increasing the high temperature soaking time and the temperature has no beneficial effect on the coalescence of the metal. The failure of the process is almost certainly due to the presence of a tenacious skin of the oxide or oxychloride on the surface of the metal. An oxide film is probably formed in the fluoride reaction but the fluoride flux dissolves it and keeps the metal surface clean. The cerium chloride–lithium reaction appeared to be initiated at a similar temperature to that at which the fluoride reaction occurred, but with a considerably greater liberation of heat: $CeCl_3 + 3Li \rightarrow 3LiCl + Ce + 44{\cdot}0$ kg.-cal./g.-mol. of $CeCl_3$ at 400°C.[110]

Mixtures of lithium and organic halogen compounds are sensitive to impact: the bromo-and iodo-derivatives are rather more reactive than the chloro-compounds, but the differences are not always considerable. It is suggested that the explosive properties of such mixtures may be explained by the formation of small amounts of highly explosive compounds, such as halogen acetylenes, which cause the explosive decomposition of the entire system. In Table II the minimum impulse (metres × kg.) required to cause explosion is given in Arabic figures, the number of explosions in five tests is shown by the figures in brackets and the strength of the detonation is denoted by I, very feeble, II feeble and III moderate.[111,112]

TABLE II.- EXPLOSIVE PROPERTIES OF MIXTURES OF LITHIUM WITH ORGANIC HALOGEN COMPOUNDS

CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4	$CHBr_3$	CBr_4	CH_2I_2	CHI_3
–	2·5(5)I	1·0(5)II	0·8(5)II	0·8(5)III	0·8(5)III	1·5(5)I	1·0(4)II

A recent explosive reaction between lithium and carbon tetrachloride has been described. In order to sample lithium metal from a billet for nitrogen analysis, without exposing the metal to the nitriding action of the atmosphere, attempts were made to cut the billet under carbon tetrachloride. Thin slices of lithium ($\frac{1}{8}$–$\frac{1}{16}$ in.) had already been held under carbon tetrachloride with metal fingers and shaken for some time without incident. A 2·5 in. thick lithium billet was then cut under carbon tetrachloride and as the shear blade touched the metal to make the fifth cut a violent explosion occurred accompanied by a bright yellow flame. Only the faintest mark of the blade was visible on the billet on later inspection. At the time of the explosion the metal had not been exposed to the air in any way and the carbon tetrachloride was very dry; the reaction continued with much crackling and flaming until the carbon tetrachloride was drained from the tank. The main products of the reaction as far as could be identified were carbon and lithium chloride; no smell of phosgene was observed. Large cavities were eaten into the metal. The only peculiar observation made during the first four cuts was that during cutting a few bubbles were evolved from around the cutting edge, and were attributed to local heating from shearing of the metal. The operators of the

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shears and two men standing five feet away received burns to the face and other parts.[113]

In the molten state, lithium attacks carbides, silicates, rubber and plastics.[109] The bottom of a porcelain tube, 2 mm. thick, was completely destroyed in 7·5 min. when lithium was heated in the tube at 465° C.[114] The attack on vitreous silica at 250° C. is very rapid and the product of the reaction is believed to be lithium metasilicate, Li_2SiO_3.[115] A special glass has been used in the preparation of lithium metal and has proved to be sufficiently resistant to attack to permit lithium to be cast, provided the metal is solidified rapidly in say ten to twenty seconds after running it into the moulds. This glass contains 2·3% SiO_2, 26·8% B_2O_3, 29·6% Al_2O_3, 35% BaO, 4·4% Na_2O and 1·9% K_2O.[116] Lithium weakens the bonding between oxygen and cobalt, thus reducing the intensity of the blue colour of silicate glass.[117] The appearance, chemical constitution, hardness and electrical conductivity of non-metallic articles containing silica, such as glasses and ceramics, can be altered without change of form or size by heating to 700–900° C. in contact with reducing metals such as lithium, for a sufficient time to transform *in situ* a substantial portion of the siliceous part of the articles into a new material having a metallic appearance. Particles of the metal oxide are embedded in a matrix of an alloy of the metal with silicon.[118]

It is postulated that alkali metals can assume a covalency of four in glasses by accepting co-ordinate links from lone pairs of electrons from oxygen in the silicate network. Experimental work on amber coloured glass shows that when constant amounts of colouring agents are present (iron oxide, sulphur and carbon), the depth of colour is increased when silica is replaced by soda and a similar effect obtained when sodium oxide is replaced with lithium oxide. Replacement of sodium oxide with potassium oxide produces a decrease in depth of colour and further addition of this oxide, at the expense of silica, causes the colour to become paler still until the potassium oxide content is 20%. Further replacement then causes a deepening of colour, a phenomenon which requires further investigation. It is assumed that a deepening of colour is produced by a process analagous to reduction and that with the exception of the special effect of zinc oxide, a decrease in depth of colour is due to an oxidation effect. The alkali metals arranged in order of increasing reducing power (*i.e.* increased basicity) are potassium, sodium, lithium. The colour of selenium-pink glasses changes from brownish pink to bluish pink by replacing sodium oxide with potassium oxide, *i.e.* there is an increase in the oxidizing nature of the batch.[119]

Alkali-metal dispersions which are stable against settling and agglomeration in which the dispersed metal does not exceed 50 μ in size, are obtained by preparing an emulsion of finely divided molten particles of an alkali metal in an inert liquid hydrocarbon having a boiling point above the melting point of the metal in the presence of an emulsifying agent. Lithium, sodium, potassium, rubidium and caesium and alloys of these metals may be used. Emulsifying agents are complex addition products formed between two distinct types of component compounds and are (1) of the general formula, MOR, where M is an alkali metal and R an aliphatic, *cyclo*aliphatic, or aromatic radical and (2) alkali metal organic compounds in which an alkali metal is directly attached to an allylic residue, *i.e.* compounds having at least one residue of the structure C:CCM, where M represents an alkali metal. An example for preparing sodium dispersions is given in Sect. XXV. The unusually finely divided form of the metal makes the dispersions useful as additives for Diesel fuels of inferior ignition characteristics, the effect being to increase the cetane number of the fuel.[120]

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REACTIONS OF LITHIUM IN LIQUID AMMONIA

Before describing the specific reactions observed in lithium solutions in liquid ammonia, a brief account of the general behaviour of the alkali metals in this solvent will give some idea of the types of reactions that may occur. There is reasonable evidence to support the view that in liquid ammonia the alkali metals are ionized according to the equation: $M \rightleftharpoons M^+ + e^-$, and that in dilute solutions the electrons are associated with ammonia molecules: $e^- + n\,NH_3 \rightarrow e^-(NH_3)_n$. Since reduction involves the addition of electrons to a given atomic system, it is apparent that such metal solutions are eminently suitable as reducing agents. An atom of sulphur is reduced to a negative ion: $S + 2e^- \rightarrow S^{--}$; $2M^+ + S^{--} \rightarrow M_2S$. A positive ion is reduced to a neutral atom: $Ag^+ + Br^- + M^+ + e^- \rightarrow Ag$ (solid) $+ M^+ + Br^-$. In a reaction of this type the metal formed may be reduced to a lower state of oxidation, it may catalyze the reaction between the alkali metal and ammonia yielding the amide and hydrogen, it may react with the amide so formed, or it may take part in no further reaction. The course of reactions of the following type: $K^+ + e^- + Na^+ + Cl^- \rightarrow KCl$ (solid) $+ Na^+ + e^-$, is determined by solubility relationships. Negative ions may be further reduced: $2M^+ + S_n^{--} + 2M^+ + 2e^- \rightarrow M_2S$ (solid) $+ 2M^+ + S_{(n-1)}^{--}$; $2M^+ + NO_2^- + e^- \rightarrow M_2NO_2$ (solid).

Liquid ammonia has many advantages as a medium in which to carry out reducing reactions: it is a solvent for numerous inorganic and organic substances and such solutions, containing free electrons when the alkali metals are present, provide an infinite surface for reaction; it is only on rare occasions that an excess of the reducing agent is necessary, and many reactions can be followed visually because the initial intense blue colour of the metal solution is discharged as the reaction proceeds. In the absence of metal catalysts and at ordinary temperatures the rate of interaction of the alkali metals with liquid ammonia is negligible compared with the rates of the reactions now under consideration. Where by reason of solubility relationships liquid ammonia is unsuited to a given reaction, the simple amines methylamine and ethylamine may be used. Well documented reviews are available on the reactions of inorganic and organic substances in liquid ammonia and amine solutions of the alkali metals.[1-3]

In the presence of metal catalysts and at elevated temperatures the alkali metals react with liquid ammonia forming the metal amide and liberating hydrogen. The effect on the usual materials of plant construction has been investigated for solutions of sodium in liquid ammonia.[4]

The reactions of lithium in liquid ammonia with the elements oxygen, sulphur, selenium, tellurium, arsenic, antimony and phosphorus have already been described (see pages 70-77). The electrolysis of lithium iodide in liquid ammonia with a platinum anode and a lead cathode results in the formation of a green solution containing lithium polyplumbide to which the formula Li_4Pb_n has been given.[5] When ammonium salts are added to lithium solutions in liquid ammonia, hydrogen and ammonia are produced and the corresponding lithium salt is obtained: $Li^+ + e^- + NH_4^+ + Cl^- \rightarrow Li^+ + Cl^- + NH_3 + H$;[6] $Li^+ + e^- + NH_4^+ + I^- \rightarrow Li^+ + I^- + NH_3 + H$.[7] Liquid hydrogen sulphide reacts with lithium in liquid ammonia solution, in the absence of air, liberating hydrogen and ammonia and forming lithium sulphide.[8] Lithium reacts vigorously with ammonium azide to give lithium azide: $Li + NH_4N_3 \rightarrow LiN_3 + NH_3 + H$.[9] The blue colour of lithium in liquid ammonia is immediately discharged when the solution reacts with a suspension of aluminium iodide hexammoniate, $[Al(NH_3)_6]I_3$, at -70°C. and the solid phase passes into solution. The initial reaction is rapid and is followed by a slow reaction differing little in speed from that of lithium on the solvent. The suggested course of the initial rapid reaction is $[Al(NH_3)_6]^{+++} + NH_3 \rightarrow [Al(NH_3)_5NH_2]^{++} + NH_4^+$; the ammonium ions are destroyed by the metal solution, $NH_4^+ + e^- \rightarrow NH_3 + H$, and the rapid reaction continues until all the aluminium is present as a soluble, relatively stable complex having the empirical formula $Al(NH_2)_{1\cdot5}I_{1\cdot5}$. The net result is the evolution of hydrogen and the accumulation of amide in solution, and the solid products isolated are found to be a mixture of ammonobasic aluminium compounds.[10] Lithium in liquid ammonia solution reacts with the diammoniate of diborane ($B_2H_6,2NH_3$) in the same solvent; on removal of the solvent a mixture of lithium borohydride, $LiBH_4$, and aminoborine, BH_2NH_2 (polymeric) is obtained. Stoicheiometrically the overall process is represented by the following equations: (1) Li (soln.) + $B_2H_6,2NH_3$ (soln.) = LiB_2H_8N (soln.) + $0\cdot5H_2$ + NH_3; (2) LiB_2H_8N (soln.) = $LiBH_4$ (solid) + BH_2NH_2 (polymeric). The formula, LiB_2H_8N accords with the stoicheiometry but does not imply a structure or a particular species. The borohydride and aminoborine are probably present in the solution before removal of solvent because at -78°C. lithium borohydride tetrammoniate appears as the solid phase immediately upon removal of the solvent. If this is the case, the reaction of lithium with the diammoniate of diborane should be expressed as: Li (soln.) + $B_2H_6,2NH_3$ (soln.) = Li^+ (soln.) + BH_4^- (soln.) + BH_2NH_2 (soln.) + NH_3 + $0\cdot5H_2$, and the removal of solvent as: Li^+ (soln.) + BH_4^- (soln.) + BH_2NH_2 (soln.) = $LiBH_4$ (solvate) + BH_2NH_2 (polymeric). The borohydride is separated by excess metal and polymeric aminoborine by the use of ether as solvent. Ammonolysis of the aminoborine occurs with the production of hydrogen unless the solvent is removed at the lowest possible temperature: $BH_2NH_2 + xNH_3 = xH_2 + BH_{2-x}(NH_2)_{1+x}$.[11] The reaction between boron trifluoride and lithium in ethylamine solution proceeds almost quantitatively, three atoms of hydrogen being evolved for each molecule of the trifluoride: $BF_3 + 3C_2H_5NH_2 + 3Li \rightarrow B(C_2H_5NH)_3 + 3LiF + 3H$.[12] Liquid ammonia solutions of the complex, BF_3,NH_3, have been titrated with liquid ammonia solutions of the alkali metals in an apparatus which permits the quantitative recovery of all products. Treatment of solutions of the complex with excess alkali-metal solution, followed by back titration with ammonium iodide, has also been carried out. The titrant and moles of titrant per mole of BF_3,NH_3 by forward titration are Li, 2·91; Na, 2·50; K, 1·00; Cs (back titration), 1·03; KNH_2, 2·6. A straightforward difference in stoicheiometry of the reactions with different alkali metals is shown and equations given are in agreement with experimental results. For lithium the reaction is expressed by: $6Li + 2BF_3,NH_3 + 2NH_3 \rightarrow 6LiF + (NH_2)_2BNHBNH + 3H_2$.[13] Lithium carbonyl, LiCO, is obtained as a white powdery substance when pure dry carbon monoxide is passed through a solution of lithium in liquid ammonia; both air and moisture must be rigidly excluded because of the highly reactive nature of the product which detonates violently with water with instant ignition of the gaseous products, leaving a residue of carbonate and carbon.[14]

Reactions of lithium in ammonia with arsine, phosphine and sodium nitrite have already been described (see page 77).

Dipotassium ammonolithiate, $LiNK_2,2NH_3$ or $LiNH_2,2KNH_2$ or $[Li(NH_2)_3]K_2$, is formed as a greyish but well crystallized solid when lithium and potassium, in the presence of a minute portion of platinum black, are allowed to react with liquid ammonia. The ammonolithiate decomposes in the presence of ammonium salts of the oxygen and halogen acids to give the corresponding salts of lithium, potassium and ammonium. Monorubidium ammonolithiate, $LiNHRbNH_3$ or $LiNH_2RbNH_2$ or $Li(NH_2)_2Rb$, is formed in a similar manner. Rubidium with a minute portion of platinum black is allowed to stand with liquid ammonia until the blue colour of the metal solution disappears and a liquid ammonia solution of lithium is then poured on to it. The ammonolithiate so formed is a greyish crystalline solid. These reactions must be carried out in the absence of air and water.[7] The rates of solution of the alkali metals in liquid ammonia and the rates of the ensuing reactions with nickel bromide, $NiBr_2$, are too rapid for accurate measurement, but both rates increase from lithium to cæsium. The reactions yield nickel and the catalytic activity per unit area of the nickel produced by the reducing metals lithium, sodium, potassium, cæsium is substantially constant.[15]

Numerous organic reactions have been studied in liquid ammonia or ethylamine solutions of lithium and a brief account of some of these is given below.

Saturated hydrocarbons are not attacked by the alkali metal solutions but hydrogen is displaced from acetylene with the formation of the metal salt: $C_2H_2 + Li \rightarrow C_2HLi + H$. Attempts to isolate the acetylide by heating in a high vacuum at 120°C. produce a mixture containing 82% of lithium carbide and 17·6% of the acetylide.[16] The aromatic hydrocarbons, benzene, toluene and xylene, do not react with the alkali metal solutions and may therefore be used as diluents or as solvents for a solid reactant.[1]

Free radicals usually react with the electrons in the alkali metal solutions to form ions: thus triphenylsilicyl gives an intense red solution with lithium in ethylamine from which a crystalline solid, $(C_6H_5)_3SiLi$, may be isolated.[17] Triethylsilicyl does not react with lithium, but the metal catalyzes the reaction: $(C_2H_5)_3SiH + C_2H_5NH_2 + Li \rightarrow (C_2H_5)_3SiNHC_2H_5 + H_2 + Li$.[18] Triethylgermanyl forms lithium triethylgermanide, $LiGe(C_2H_5)_3$, in ethylamine solution and the product is partially aminolyzed in this solvent to give triethylgermane, $(C_2H_5)_3GeH$, and in ammonia is completely ammonolyzed.[19] Monomethyl- and monoethyl-germanes react in almost equivalent amounts with lithium in ethylamine solution to give CH_3GeH_2Li and $C_2H_5GeH_2Li$. On warming to room temperature the white solids become yellow and hydrogen is evolved; secondary reactions also occur and ethane is given off. Ethyl*iso*amylgermane also reacts with lithium in ethylamine but in this case the lithium salt has not been isolated.[20] Triphenylgermanyltriethylsilicon with lithium in ethylamine gives an equimolecular mixture of lithium triethylsilicide and lithium triphenylgermanide.[18] Trisubstituted derivatives of boron and gallium also react with lithium in ethylamine. With trimethylboron the reaction is quantitative: $(CH_3)_3BC_2H_5NH_2 + Li \rightarrow (CH_3)_3BC_2H_5NHLi + H$; concentrated solutions of the salt are unstable and two molecules of methane are produced per molecule of salt. Tributylboron reacts similarly and again concentrated solutions of the lithium salt decompose evolving butane.[21] Trimethylgallium reacts according to the following equations: $Li + (CH_3)_3GaC_2H_5NH_2 \rightarrow (CH_3)_3GaC_2H_5NHLi + H$; $2Li + 2(CH_3)_3GaC_2H_5NH_2 \rightarrow [(CH_3)_3Ga]_2^{--} + 2Li^+ + 2C_2H_5NH_2$; $Li_2[Ga(CH_3)_3]_2 + 2C_2H_5NH_2 \rightarrow 2LiC_2H_5NHGa(CH_3)_2 + H_2$: 39·8% of the gallium reacts according to the first equation, 61·2% according to the second. The product of the first reaction is stable in the dry state as well as in ethylamine solution but the product of the second is measurably stable only at -33° C. and breaks down on removal of the solvent.[22]

Organohalides of silicon, germanium and bismuth react with lithium solutions in ethylamine. Triphenyl- and triethyl-silicon bromides give respectively $(C_6H_5)_3SiC_2H_5NH_2$ + LiBr and $(C_2H_5)_3SiNHC_2H_5$ + LiBr + H.[18] Diphenylgermanium chloride forms lithium chloride and a resinous material approximating to the composition of diphenylgermanium.[23] Triethyl germanium chloride, bromide, fluoride and iodide react as follows: $2(C_2H_5)_3GeX + 2Li \rightarrow 2LiX + [(C_2H_5)_3Ge]_2$; $[(C_2H_5)_3Ge]_2 + 2Li \rightarrow 2LiGe(C_2H_5)_3$. In ethylamine solution, and more so in ammonia solution, the lithium salt ammonolyzes: $LiGe(C_2H_5)_3 + NH_3 \rightarrow (C_2H_5)_3GeH + LiNH_2$.[19] Organobismuth compounds react with lithium in liquid ammonia forming highly reactive deep red coloured compounds of the type R_2BiLi which decompose slowly to salts, R_3Bi, but are sufficiently stable to react promptly with organohalides.[24]

In its behaviour towards alcohols lithium resembles the alkaline earth metals in that its reactions are slow compared with those of the other alkali metals. With methanol the decolorization of a lithium solution in liquid ammonia is followed by the immediate precipitation of lithium methoxide which is insoluble at -50°C. even in an excess of the alcohol: $CH_3OH + LiNH_3 \rightarrow CH_3OLi + NH_3 + H$. Lithium ethoxide, on the other hand, is very soluble in ethyl alcohol; if the ammonia is driven off without decantation a crystalline mass is obtained which loses alcohol slowly in the cold but rapidly at 100°C., leaving a white amorphous mass of the ethoxide. Similar reactions occur with *iso*butyl and *iso*amyl alcohols. Glycol gives the monolithium derivative, $C_2H_5O_2Li$, which may be transformed rapidly and completely into the dilithium salt by heating at 170-200°C. Lithium differs from the other alkali metals in that it gives the dilithium salt of erythritol and mannitol and not the monoderivative, and in this respect it resembles the alkaline earth metals.[25] In the presence of ethyl alcohol, lithium solutions in liquid ammonia reduce phenolic ethers, giving in some cases remarkably good yields of the reduction products, whereas sodium and potassium under similar conditions have failed to react. This is probably due to the higher normal reduction potential of lithium in liquid ammonia (Li, -2·99 V.; Na, -2·59 V.; K, -2·73 V.), to its high solubility and low molecular weight which permit higher concentrations to be used, and to the fact that the reaction between lithium and ethyl alcohol is slower.[26] By means of the lithium-ammonia-alcohol procedure it has been possible to convert 11-ketosteroids into the corresponding 11-α-hydroxycompounds; the diethyleneketal of cortisone has been transformed into the practically pure 11-α-hydroxide compound, and 19-nortestosterone and 19-norandrostenedione have been synthesized from estrone.[27-29]

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ORGANOLITHIUM COMPOUNDS

The first organolithium compound was made by Schlenk and Holtz[1] in 1917 and since that date so much work has been devoted to the study of organolithium compounds that their usefulness is now comparable with that of Grignard compounds. They are the most reactive of the organometallic compounds.

The lithium alkyls can be prepared by the method of Schlenk and Holtz, namely, by reaction between lithium and a mercury dialkyl: $2Li + HgR_2 \rightarrow 2LiR + Hg$, but are more usually obtained by the direct metallation process of Ziegler and Colonius[2] in which lithium reacts with an alkyl halide: $2Li + RHal \rightarrow RLi + LiHal$. A third alternative is the indirect metallation process of Gilman[3,4] and Wittig[5] in which an easily prepared alkyl-lithium (e.g. *n*-butyl-lithium) is allowed to react with a bromo-compound which does not itself react directly with lithium: $BuLi + C_6H_5(OMe)Br \rightarrow BuBr + C_6H_5(OMe)Li$.

Some organohalides that react only sluggishly with magnesium give good yields of the lithium derivative: p-bromodimethylaniline gives a 95% yield of p-lithium dimethylaniline,[6] and certain alkenyls which do not form Grignard reagents react with lithium to give the metal compound: $(CH_3)_2C = CHBr + 2Li \rightarrow (CH_3)_2C{=}CHLi + LiBr$.[7] On the other hand, some halides which form Grignard reagents with great ease, for example, polyhalogen-aryl compounds such as p-chlorobromobenzene, are substantially unaffected by lithium.[8]

Halogenated naphthalene with the halogen in the alpha position gives lithium naphthyl, $C_{10}H_7Li$, which may be converted into homologues of naphthalene; when the halogen is in the beta position, binaphthyl is obtained.[9]

Perfluoroalkyl iodides react with lithium in the presence of a solvent to form lithium perfluoroalkyl compounds.[10]

Although many lithium alkyls have been used in synthetic experiments, few have been isolated. Lithium methyl is an anomalous compound, being a white amorphous powder decomposing and burning explosively in air and decomposing without melting on heating; it is insoluble in many organic solvents. On the other hand, lithium ethyl is a colourless crystalline solid which melts to a clear liquid at 95°; it can be purified by sublimation[11] and is soluble in benzene and many other solvents. Higher lithium alkyls constituting a fairly representative series have been prepared, but only occasionally isolated.[12-27]

Most lithium alkyls are now prepared in light petroleum[29] or benzene solution;[28] in ethyl ether they must be used shortly after preparation as they react with this solvent to give saturated and unsaturated hydrocarbons and a

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lithium alkoxide: e.g. $(Et)_2O + LiEt \rightarrow LiOEt + C_2H_6 + C_2H_4$. Lithium alkyls (except the methyl compound) have low dipole moments[30] and give non-conducting solutions in benzene,[31] from which a covalent structure is deduced and a resemblance between the C-Li and C-F bonds is established qualitatively.

Among the important reactions of lithium alkyls is the formation of fully alkylated metal compounds directly from the anhydrous metal chloride. Thus, gold trichloride and lithium ethyl yield triethyl gold:[32] $AuCl_3 + 3C_2H_5Li \rightarrow Au(C_2H_5)_3 + 3LiCl$. Similar reactions have been observed with germanium[33] and thallium,[34] whilst the use of lithium aryls has enabled the whole series of pentaphenyl derivatives of the P, As, Sb, Bi family to be obtained[35,36] e.g. Ph_5P which has m.p. 124° or Ph_5Bi, m.p. 100–104°. Gilman and his co-workers[37] were able to synthesize the theoretically very important compound $(C_6H_5)_3C.Si(C_6H_5)_3$ analogous to hexaphenylethane, by the reaction of triphenylmethane with a lithium alkyl to give lithium triphenylmethyl: $(C_6H_5)_3CH + LiR \quad RH + (C_6H_5)_3CHLi$. The latter compound reacts with triphenyl silicon chloride to give the required substance: $(C_6H_5)_3CHLi + (C_6H_5)_3SiCl \rightarrow (C_6H_5)_3C.Si(C_6H_5)_3 + LiCl$. This analogue of hexaphenylethane is colourless and highly stable, m.p. 340–345°, showing no tendency to ionize across the C–Si bond.

The ability of lithium alkyls to react with double bonds is almost unique and makes them very valuable synthetic agents.[38] The reaction between ethylene and lithium butyl gives a series of lithium alkyls: these react with formaldehyde to give the primary alcohol series C_7–C_{13}, approximately in the proportions 5: 5: 3: 1. In this way, by using different lithium alkyls, the whole homologous series of paraffin alcohols can be obtained.[39]

$$\begin{array}{rl} C_2H_4 + BuLi \rightarrow & C_6H_{13}Li + CH_2O \rightarrow C_7H_{15}OH \\ C_2H_4 \downarrow & C_8H_{17}Li + CH_2O \rightarrow C_9H_{19}OH \\ C_2H_4 \downarrow & C_{10}H_{21}Li + CH_2O \rightarrow C_{11}H_{23}OH \\ C_2H_4 \downarrow & C_{12}H_{25}Li + CH_2O \rightarrow C_{13}H_{27}OH \end{array}$$

Further, lithium alkyls will add to the $-N{=}CH-$ linkage in pyridine and analogous compounds leading to $-N{=}\underset{|}{C}-R$ compounds, R being the alkyl from the organometallic reactant.

Reaction of lithium alkyls with double bonds, followed by the action of carbon dioxide on the product, is an excellent and expeditious way of synthesizing complex carboxylic acids:[40-42] $(C_6H_5)_2C{=}CH_2 + Li(C_3H_7) \rightarrow (C_6H_5)_2CLi\text{-}CH_2C_3H_7 + CO_2 \rightarrow (C_6H_5)_2C(COOH)C_4H_9$. With dimethylbutadiene, butadiene, isoprene and piperylene,[44] two atoms of lithium react, leading to the formation of large unsaturated hydrocarbon molecules.

It is not possible here to list all the applications of the lithium organic compounds in organic syntheses, but the following are exceptional as being reactions which can be carried out expeditiously only by the action of lithium derivatives.

(1) The synthesis of azaporphins direct from *o*-phthalodinitrile.[43]

(2) The use of lithium alkenyls, particularly lithium vinyl, $CH_2{=}CHLi$, in organic syntheses such as the formation of phenylpropenylcarbinol, $C_6H_5.CHOH.CH{=}CH\text{-}CH_3$, from propenyl lithium $CH_3CH{=}CHLi$ and benzaldehyde.[45-48]

(3) Synthesis of *cyclo*hexenyl derivatives from bromo*cyclo*hexenyl compounds without loss of unsaturation.[49,50]

Thus, lithium *cyclo*hexenyl will yield phenyl*cyclo*hexenylcarbinol with benzaldehyde, or decahydrofluorenone with bromo-*cyclo*hexene.

(4) The lithium alkynes, e.g. $CH{\equiv}CLi$ are readily formed; they are much more soluble than the analogous sodium compounds and give better yields[51] of -yne compounds, e.g. $RC{\equiv}CLi + BrBu \rightarrow RC{\equiv}$

$C(CH_2)_3CH_3$, a reaction which has considerably facilitated the total synthesis of vitamin-A.[52]

Lithium aryls are easily obtained by the direct metallation of aryl chlorides or bromides; and in many cases where Grignard compounds are formed from chlorides only with great difficulty, lithium reacts readily. Where, owing to steric factors, lithium will not react directly (e.g. with chloromesitylene); indirect metallation with lithium propyl is usually effective.[53-58] Indirect metallation by displacement of hydrogen from a benzene ring is possible in some instances; e.g. anisole, C_6H_5.OMe, yields the *o*-lithium derivative, C_6H_4(Li)OMe, with phenyl lithium.[59-61] One of the more unusual reactions of phenyl lithium is with nitrous oxide giving first C_6H_5N=N.OLi and then a series of decomposition products.[62]

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SECTION V

LITHIUM ALLOYS

By MRS. F. DICKINSON

The term 'alloy' has been defined as 'a mixture with metallic properties, composed of two or more elements of which one at least is a metal'. Alloys differ not only according to the elements of which they are composed but also according to the crystal structure and the distances between the atomic centres in the crystal lattice. Usually, face-centred cubic systems are more ductile but less strong than body-centred cubic alloys; hexagonal and other non-cubic alloys are not generally as malleable as cubic structures. The properties of an alloy are also determined to a large extent by the distribution of phases in the system. The high strength of age-hardened alloys is accounted for by the fine dispersion of a second phase throughout the alloy; where, on annealing, the second phase is distributed as coarse particles, the strength is not nearly so great. Most solid solutions are of the 'substitutional' type in which one kind of atom in the crystal structure is replaced by other metal atoms at random; the 'interstitial' type of solid solution is one in which atoms of small radii are accommodated in the interstices of the lattice of the other metal. Only when the components have the same crystal structure is complete solid solubility possible; the greater is the difference in atomic size, the more limited is the solid solubility, and no example of complete solid solubility is known where the difference in atomic radii of the metals is greater than 15%. A metal of lower valence tends to dissolve one of higher valence to a greater extent than vice-versa, and generally metals having the same valence in the alloy as in their usual compounds exhibit greater solubility than those having different valencies. The greater is the difference in atomic size and valence, the steeper is the solidus curve and the greater the freezing range; also the farther apart are the metals in the electrochemical series, the less likely are they to form solid solutions with each other. When metals combine with each other according to their normal valencies they form 'valence compounds'. 'Electron compounds', on the other hand, are phases with wide ranges of homogeneity and are sometimes referred to as intermediate phases rather than compounds; their crystal structures are determined by the number of valence electrons in the alloying atoms. In the compound Cu_5Sn, for example, the alloying valence of copper is one and that of tin is four; the total number of valence electrons is nine and, since there are six atoms altogether, the electron-atom ratio is 9:6 or 3:2. This ratio is found in compounds which have the beta-brass or beta-manganese structure; for gamma-brass the ratio is 21:13 and for the hexagonal structure of epsilon-brass it is 7:4. Many intermetallic compounds are such that small atoms fit interstitially between the metal atoms in the structure, but these compounds should not be confused with interstitial solid solutions in which the small atoms are distributed at random. The essential difference between a solid solution and a compound is that in the former the atoms of the different metals are distributed at random on the lattice points, but in a compound, atoms of each kind occupy assigned lattice points. When a shift of the atoms from random to assigned positions occurs, the compounds so formed are described as super-lattice compounds and the above type of change is one of order-disorder.

With regard to the physical properties of alloys, the thermal and electrical conductivities of a solid solution are less than those of the pure metal. Matthiessen's rule states that as small amounts of an alloying element are added in solid solution to a metal, the increase in resistance is independent of temperature; for mixtures of insoluble phases, the resistivity follows the law of mixtures. Generally, the lattice parameter and density are increased by a heavier metal in solid solution and decreased by a lighter one. Attraction between unlike atoms causes the lattice to be generally slightly more compressed than the law of mixtures predicts. The added element in interstitial solid solutions always expands the lattice but the effect on density is slight. The law of mixtures generally applies to the specific heat and coefficient of thermal expansion, but not in the case of the iron–nickel system. Some alloying elements stabilize a particular allotropic modification whereas others cause it to disappear. In the absence of compound formation, the heat of mixing is generally small, sometimes positive, sometimes negative, but when stable compounds are formed, the heat of mixing is positive and may be large. Shrinkage from the liquidus to solidus and from solidus to room temperature is important in the control of sound castings; fluidity is also important. In their introduction to the study of alloys Kirk and Othmer[1] also discuss the mechanical properties of alloys, their corrosion resistance, and treatments such as melting, casting, sintering, hot working, cold working, surface treatments and heat treatment.

The following methods for the detection of intermetallic compounds have been discussed: *X*-ray investigation, thermal expansion, the determination of electrical resistance as a function of temperature and the examination of magnetic properties as a function of concentration and temperature.[2]

In the following account of the behaviour of lithium with other metals, percentage composition refers to weight per cent. unless otherwise stated.

Lithium and sodium are practically immiscible; since, however, the melting point of lithium is depressed by the addition of sodium and that of sodium by the addition of lithium, the metals must be soluble in each other to some extent. According to earlier workers[3-5] the melting point of sodium is lowered by about 2°C. by 0·5% of lithium and that of lithium from 179°C. to 162°C. by 7% of sodium. Böhm and Klemm give the lowering of the melting point of sodium (97·5°C.) as 6° to 7°C. and that of lithium (178°C.) as 12°C. No compound of lithium and sodium has been reported.[6] In an investigation of the effect of geometrical factors on the stoicheiometric formula of metallic compounds it is observed that in the system, Na–Li, where the radius ratio is 1·22:1, no compound is formed.[7] A series of spectrograms has been obtained with lithium maintained at 850°C. and sodium at 435°C., 460°C., 485°C. and 510°C. and also with a constant high sodium vapour pressure, with increasing lithium vapour pressure; no evidence of bonds attributable to a sodium–lithium molecule has been found in the region of 3000 A. to 8000 A. and this is the only binary compound of the alkali metals which has not been found.[8] The phase diagram of the sodium–lithium system has been more recently investigated to evaluate the solubility of molten lithium in sodium. The metals were melted in a mild steel crucible of 10-10 low-carbon steel, which was tapered at its lower end and was open to another crucible through a small orifice. The two crucibles were fitted into an apparatus which could be filled with argon and evacuated, and means were provided to determine the temperature of the melts in the lower crucible; the molten metals in the upper crucible were freed from oxide by evacuating the system under argon when an intact 'skin' of oxide remained in the upper crucible and the molten metals passed through to the lower one. The liquidus and solidus of a 50 vol.-% alloy, *i.e.* 37 wt.-% of lithium, were determined by thermal analysis as also was the melting point of lithium. The composition of the two liquid layers in the immiscibility region was determined by chemical analysis, and the limits of the immiscibility region were calculated from the available experimental data by applying Van Laar's equations for activity coefficients in a two component solution. It was found that the freezing point of lithium was reduced from 179·4°C. to 171°C. by the addition of 3·3 atomic-% of sodium and that at 171°C. sodium and lithium formed two immiscible liquid phases of composition 3·3 and 86·9 atomic-% of sodium in equilibrium with solid lithium. The eutectic composition of the sodium-rich alloy was at 96·3 atomic-% of sodium and the eutectic temperature was 93·4°C. The calculated compositions of the two liquid layers of the complete immiscibility loop are given in Table I.

TABLE I. - COMPOSITION OF LITHIUM-SODIUM ALLOYS

Equilibrium Temperature °C.	Composition of Phases, Mole Fraction			
	Top Layer		Bottom Layer	
	Li	Na	Li	Na
171	0·967	0·033	0·131	0·869
200	0·951	0·049	0·173	0·827
250	0·910	0·090	0·270	0·730
300	0·824	0·176	0·424	0·576
320	0·743	0·257	0·529	0·471
327·3	0·66	0·34	0·66	0·34

Diagrams of the apparatus and of the phase system are given.[9] Subsequently the same authors have said that 3·8 atomic-% of sodium reduces the freezing point of lithium from 179·4 to 171°C. Howland and Epstein have studied the sodium–lithium phase system by thermal analysis in the liquid and solid regions to temperatures in excess of 400°C. They find that two liquid phases separate at 170·6°C. with compositions of 3·4 and 91·6 atom-% of sodium. The critical solution is 442° ± 10°C. at a composition of 40·3 atom-% of sodium. (Salmon and Ahmann[9] by extrapolating their low temperature data obtain a critical solution temperature of 379°C. at a composition of 35 atom-% of sodium). The freezing point of pure lithium is found by Howland and Epstein to be depressed from 180·5°C. to 170·6°C. by the addition of 3·4 atom-% of sodium and the freezing point of pure sodium from 97·8° to 92·2°C. by the addition of 3·8 atom-% of lithium. One liquid phase exists in equilibrium with pure lithium from 170·6°C. to 92·2°C. Correlation of the experimental data with the Scatchard–Hildebrand regular solution model using the Flory–Huggins entropy correction is discussed and the suggestion is made that instead of the liquid phase containing only the species lithium and sodium, there may be some chemical combination. Preliminary experiments by *X*-ray examination and other techniques have given no indication of anything but pure sodium and lithium as the solid separated phases, although admittedly the presence of a solid solution region of no more than a few tenths of an atom-% would probably have escaped detection.[10]

Masing and Tammann,[4] in their investigation of the lithium-potassium system, found that the melting point of one of the alkali metals was lowered by the addition of the other, but Böhm and Klemm[6] showed that the melting point of the two alkali metals in the systems lithium–potassium, lithium–rubidium and lithium–caesium remained unaltered by the addition of one of the metals to the other, the metals in the above system being almost completely

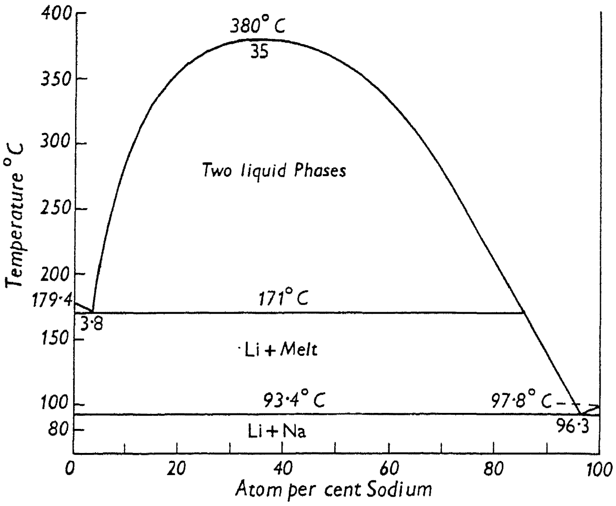

FIG. 1. EQUILIBRIUM DIAGRAM OF THE LITHIUM–SODIUM SYSTEM.[9]

immiscible. The vapours of two dissimilar alkali metals form diatomic molecules such as LiK, LiRb and LiCs.[11] Values for the heat content and entropy at temperatures from 400° to 2000°K. for LiK (gas), LiRb (gas) and LiCs (gas) have been tabulated and the following equations given for the heat content:-

$$\text{LiK (gas):}\quad H_T - H^{\text{gas}}_{298\cdot16} = 8{\cdot}94T + 0{\cdot}14 \times 10^5T^{-1} - 2713$$

$$\text{LiRb (gas):}\quad H_T - H^{\text{gas}}_{298\cdot16} = 8{\cdot}94T + 0{\cdot}11 \times 10^5T^{-1} - 2702$$

$$\text{LiCs (gas):}\quad H_T - H^{\text{gas}}_{298\cdot16} = 8{\cdot}94T + 0{\cdot}09 \times 10^5T^{-1} - 2696$$

The values obtained from the above equations are accurate to 1% between 298$^{\text{c}}$ and 2000°K.[12] The possible effect on solid solubility relations of the mutual distortion of the electron clouds of the component ions in a binary alloy may be of importance for alloys containing small ions bearing a high charge. For dilute solutions an estimate can be made of the extra energy, Δ_{12}, associated with the solution of metal 2 in metal 1 to form an alloy.[13] In the case of solid-solution formation the variation of Δ_{12} with composition must be considered. By assuming that Δ_{12} varies linearly with composition, Henry and Raynor[14] have shown that if Δ_{12} is large, limited solid solution is to be expected, while if Δ_{12} is small, extensive or complete solid solution formation is possible. Calculations for the alkali metals taken in pairs give results in good agreement with experimental work and solid solution formation is restricted in all the possible systems to potassium–rubidium, potassium–cæsium and rubidium–cæsium, for which extensive solid solutions exist.

Lithium–copper alloys containing 1·7 to 94·01 atomic-% of lithium were prepared by Pastorello[15] by fusing the metals in nickel–chromium steel crucibles in an atmosphere of argon. Alloys containing 1·7, 9·9 and 14·38 atomic-% of lithium resembled pure copper in colour; those with higher percentages of lithium were of a colour approaching the metallic gray of lithium. All the alloys were ductile and those with a high lithium content were almost as soft as lithium itself; they were all attacked by water. An *X*-ray examination of an alloy containing 50 atomic-% of lithium showed

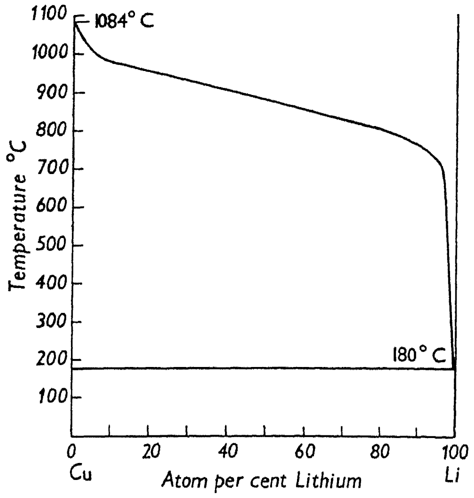

FIG. 2. EQUILIBRIUM DIAGRAM OF THE LITHIUM-COPPER SYSTEM.[15]

diffraction lines which corresponded with the normal structures of copper and lithium; no intramolecular compound and no solid solutions were formed. The depression of the melting point of copper was found to be almost linear for alloys containing 10 to 90 atomic-% of lithium, the eutectic temperature being apparently only slightly lower than the melting point of lithium. Other authors have referred to Pastorello's. work.[5,15-17] Oxygen and other inclusions and gases are removed from molten copper by treatment with approximately 0·025% of a lithium alloy, such as a 50-50% lithium calcium alloy; a molten slag of low specific gravity is produced on the surface of the melt and is not entrapped in the casting, and no new impurities are introduced. The treated copper free from oxygen and inclusions is described as lithium copper. Its crystallization temperature is raised; it can be annealed at considerably higher temperatures without its conductivity being lowered, and the resultant bright anneal is attractive in appearance. The lithium-calcium content, usually less than 0·01%, tends to protect the copper against oxidation. Lithium copper has a high density and strength and the successful development of high conductivity lithium copper has led to the industrial development of lithium alloy treatment; thus an increased electrical conductivity, averaging more than 2% greater than has been obtainable with any other deoxidizing agent, has resulted when high conductivity, high strength bronzes have been subjected to the above treatment.[18] The electrical conductivity of copper is improved by treatment with 0·002–0·03% of lithium.[19] Lithium acts as a degasifying agent in welding material consisting of 78–90% of copper, 5–9% of tin and 3–9% of zinc.[20] The effect of lithium additions to high conductivity copper, gun-metal, nickel bronze and copper–aluminium alloys has been examined.[21,22]

Lithium-silver alloys were prepared by Pastorello by heating the metals in nickel-chromium steel crucibles in an argon atmosphere. At about 500°C. fused lithium reacted violently with silver, especially when the latter was finely divided, and heat was evolved indicating the formation of intermetallic compounds. For alloys rich in lithium, it was necessary to heat to about 700°C.; for the preparation of those less rich in lithium, a temperature near the melting point of silver was required. Alloys containing 85·5 to 93·5 atomic-% of lithium were malleable; those containing 65·8 to 93·5 atomic-% of lithium gave in liquid ammonia the characteristic blue colour of lithium solutions; alloys with 48 to 52 atomic-% of lithium gave no appreciable blue colour in liquid ammonia, indicating the existence of the compound, LiAg. This compound was found to have a cubic lattice of the cæsium chloride type with a 3·225 A. and density 5·68. The presence of a second compound, Li_3Ag, was also observed. The compound, LiAg, and silver were present in alloys containing less than 48 atomic-% of lithium; two compounds, LiAg, and Li_3Ag were considered to be present in alloys with 56 to 72 atomic-% of lithium and those with 80 to 100 atomic-% of lithium were eutectic mixtures of lithium with the compound, Li_3Ag. The system was studied by X-ray analysis.[23]. By means of thermal analysis, the same author found the melting point of the compound, LiAg, to be 955°C. and that of the compound, Li_3Ag 450°C.; three eutectic points were found at 610°C., 410°C. and 180°C., corresponding respectively to the concentrations, 30, 70 and 100 atomic-% of lithium. The introduction of 0·35 weight-% of lithium depressed the melting point of silver by about 20°C. and no solid solutions were found to exist.

An X-ray study of the crystalline structure of the compound, LiAl, showed that not only had this substance the same structure as the compound, LiAg, but it also had a similar lattice constant, a 3·23 A., which agreed with the fact that silver and aluminium have substantially the same atomic diameter, 2·88 and 2·87 A. respectively.[24 25] Silvery white and finely crystalline lithium-silver alloys, containing about 50 atomic-% of lithium, were prepared by Zintl and Brauer, who confirmed the existence of the phase, LiAg, which was shown to have a beta-brass structure, but their results for the lattice constant, 3·168 ± 0·003 A., and density, 6·25, were different from those of Pastorello. The number of atoms per unit cell was 2·1; for beta-brass the number is 2. The density was considered by these workers to be too high, owing probably to the instability of the compound at ordinary temperatures, but there was no doubt that the unit cell contained two atoms.[25] According to Perlitz, the compound, Li_3Ag, has a simple cubic structure with a 9·94 A.; the unit cell contained 52 atoms and the densities for alloys containing 76·3 and 80·2 atomic-% of lithium were 3·70 and 2·35 respectively, the volume per atom for each being[5,13,21] 18·8 A^3. More recently, the lithium-silver system has been reinvestigated because the results obtained for the ternary magnesium-silver-lithium system could not be reconciled with the previously accepted equilibrium diagram for lithium-silver. The new equilibrium diagram is considerably different from that of Pastorello; the liquidus curve falls relatively smoothly from the freezing point of silver to a eutectic with 89·2 atomic-% of lithium at 145·5°C. and then rises to the freezing point of lithium. The solubility of lithium in silver, alpha phase, is 46·6 atomic-% of lithium at room temperature and 60·8 atomic-% at 317°C. The solid solubility of silver in lithium is approximately one atomic-% at room temperature and 9 at 145·5°C. The beta phase, LiAg, is formed in the composition range 50–60·8 atomic-% of lithium from the alpha phase by a reaction in the solid state; in the range 60·8 to 77·0 atomic-% of lithium it enters into equilibrium with the liquid: $\alpha \rightleftharpoons \beta$ + liquid (317°C.). The γ_3 phase is formed by a reaction in the solid state from the beta phase or by the reaction $\beta \rightleftharpoons \gamma_3$ + liquid (164°C.); at 154°C. the γ_3 phase and the liquid react to give the γ_2 phase. The γ_1 phase is formed in the solid state at higher lithium contents. The β, γ_3, γ_2 and γ_1 phases include the compositions LiAg, Li_9Ag_4, $Li_{10}Ag_3$ and $Li_{12}Ag$ respectively. The diffraction pattern of the beta phase is characteristic of the cæsium chloride structure, and at the composition LiAg the centres of the silver atoms are 3·163 kx apart. The γ_3, γ_2 and γ_1 phases appear to be closely related structurally and to possess gamma-brass structures. The intermediate phase examined by Perlitz[21]

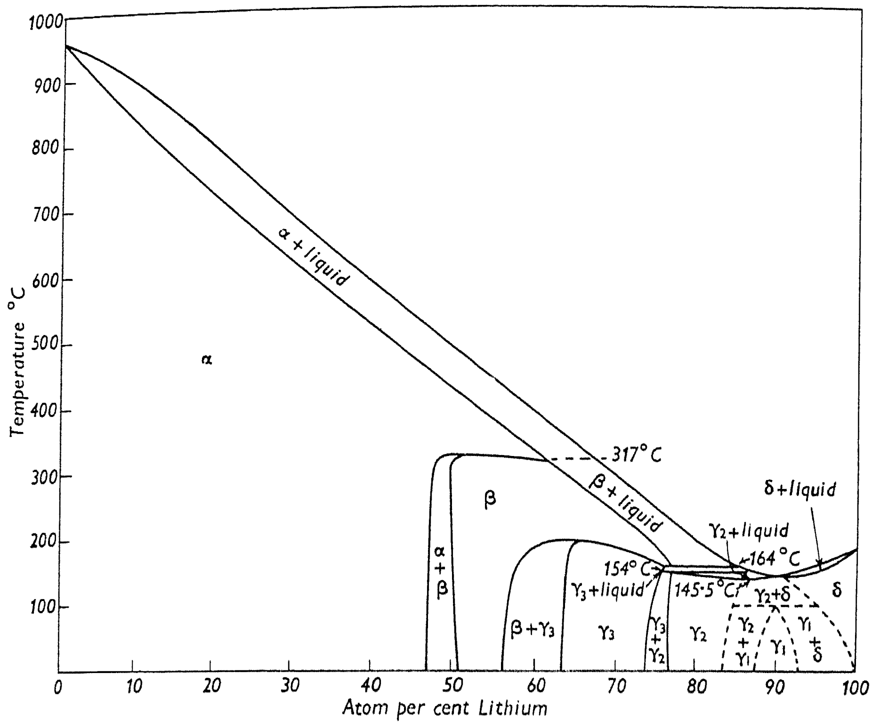

FIG. 3. EQUILIBRIUM DIAGRAM OF THE LITHIUM-SILVER SYSTEM.[27]

corresponds with the γ_2 phase, the side of the unit cell being 9·68 kx at 79·56 atomic-% of lithium. All the observed diffraction lines could also be accounted for on the basis of a face-centred cubic unit cell of side 6·50 kx. The newly discovered γ_3 phase has a large cubic unit cell of side 9·49 kx at the silver-rich composition limit. All the lines for the γ_1 phase at 91·65 atomic-% of lithium indicate a large cubic unit cell of side 9·80 kx.[27] Hume-Rothery, Betterton and Reynolds have investigated the factors controlling the composition limits of phases with the gamma-brass structure in different alloy systems and although the wide range of data agrees with accepted theory, the phase $Li_{10}Ag_3$ is an exception.[28]

In a study of the lithium–gold system, an alloy containing 44 atomic-% of lithium showed exclusively on X-ray examination the lines of a cubic lattice of dimensions approaching those of the gold lattice; another alloy with 52 atomic-% of lithium gave a new interference pattern which could not be explained. In view of the instability of the compound LiAg at room temperature, attempts were made to obtain the beta-brass structure for a similar lithium-gold compound by quenching, but without success.[5,25]

Alloys of lithium and magnesium were prepared by Masing and Tammann;[4,5] those containing 81 and 95% of magnesium were shown by microscopical examination to be homogeneous while two crystalline types were observed in an alloy containing 89% of magnesium; the liquidus curve rose from the melting point of lithium, 179°C., to that of magnesium, 650°C. By means of thermal analysis, measurement of specific conductivities of solid alloys and *X*-ray examinations, Grube, Zeppelin and Bumm[29] obtained the complete phase diagram for this system; the melting point of magnesium was 650°C. and the magnesium-rich alpha-phase was found to extend up to a concentration of 16·3 atomic-% of lithium, with a eutectic point at 587·5° and 21·8 atomic-% of lithium. By plotting lattice constants of alloys containing 20 to 40 atomic-% of lithium against atomic-% of lithium, the limits of a homogeneous region were found to extend from 21·8 to 30·8 atomic-% of lithium, and a maximum melting point, estimated as 592°C. at 28·6 atomic-% of lithium, was assumed to be the melting point of a compound Li_2Mg_5. From the maximum melting point the liquidus curve fell continuously to the freezing point of lithium at 179°C.[5,17,29] Saldau and Shamraiǐ found that magnesium forms three solid phases with lithium; the limits of the alpha-phase ranged from 10 atomic-% of lithium at 15°C. to 12·5 at 465°C. and 19 at 500°C., cutting the eutectic line at 588·2°C. and 21 atomic-% of lithium. According to microscopical examination the compound Li_2Mg_5 does not exist. A definite compound, $LiMg_2$, which melts without decomposition at 600°C., forms solid solutions (beta phase) with both its components in the region 29 to 95 atomic-% of lithium. A solid solution of magnesium in lithium, the gamma-phase, was observed between 98 and 100 atomic-% of lithium.[30,31] By microscopical examination of solid alloys and by thermal analysis Henry and Cordiano constructed an equilibrium diagram for the lithium-magnesium system. The limits of solid solubility were obtained from a series of heat-treating and quenching experiments. Their results showed that the alpha-phase was formed up to 4·9 weight-% of lithium; the beta-phase then began to appear as a broken net-work around the alpha crystals and at 10·9 to 15% of lithium only the beta-phase was visible. At room temperature the limits of the solid solubility of the alpha- and beta-phases were 4·9 and 10·6% of lithium respectively. For the alpha-phase, the solid solubility rose almost vertically from room temperature to 580°C.; for the beta-phase the solubility at 591°C. was 9·9% of lithium. Lithium and magnesium were soluble in the liquid state and partially soluble in the solid state, the curves of primary solidification intersecting at a transition point at 591°C. and 13% of lithium. A peritectic reaction between the alpha-solid solution and melt to form a lithium-rich solid solution was indicated, rather than a eutectic type.[5,16,32] By *X*-ray examination of alloys containing 6·6 to 7·3% of lithium the solubility of lithium in magnesium has been shown to be 5·7% irrespective of the temperature. The density of the alloys decreased but the Brinell hardness remained almost constant when the lithium content was increased[33] (see Table II).

TABLE II. - DENSITY AND HARDNESS OF LITHIUM-MAGNESIUM ALLOYS

Lithium wt.%	0	1·09	2·01	2·43	3·43	4·21	4·85
Density	1·741	1·700	1·670	1·657	1·628	1·607	1·589
Brinell Hardness $^{5}/_{62}$, $^{5}/_{30}$	32·0	33·2	31·5	35·0	35·0	32·3	31·9

Hume-Rothery and co-workers found that the alpha-solidus for the lithium-magnesium system was in good agreement with that of Grube, Zeppelin and Bumm[29] but distinctly lower than that given by Saldau and Shamraiǐ;[31] the eutectic temperature was found by thermal arrests to lie between 586° and 592°C., while annealing-experiments gave 588·3 to 584·8°C. The solubility of lithium in magnesium was found to be 17·0 atomic-% at the eutectic temperature, between 17·29 and 17·72 at 400°C. and 17·24 at 300°C. The beta-phase was shown to possess a body-centred cubic structure with a random arrangement of atoms at high temperatures and probably an ordered structure of the Fe_3Al type at lower temperatures. The beta-phase alloys were found to be ductile and the possibility of obtaining strong body-centred cubic alloys, lighter than magnesium, in this range of composition has been discussed.[16,34] In a later paper, Shamraĭ confirms the dystectic formation of the beta-phase, in agreement with Grube, Zeppelin and Bumm and contrary to the peritectic formation asserted by Henry and Cordiano.[32] Alloys with 21·8 and 25·75 atomic-% of lithium are distinctly of the eutectic type and the 28·7 atomic-% alloy is a single phase. On the melting diagram, the two solidus branches intersect the liquidus branch at 600°C. and 33·3 atomic-% of lithium corresponding to the composition $LiMg_2$ and not to Li_2Mg_5 as claimed by Grube, Zeppelin and Bumm. The solid solubility gap between the alpha- and beta-phases extends from 11 to 30 atomic-% of lithium; the eutectic of alpha- and beta-phases lies at about 27 atomic-% of lithium at 588°C. There is a second solubility gap between 95·7 and 97·4 atomic-% of lithium.[35] A phase diagram for compositions ranging from 0 to 33 atomic-% of lithium has been more recently investigated by Catterall. The alpha-phase has the close-packed hexagonal structure of magnesium whilst the beta-phase has the body-centred cubic structure of lithium. The solid solubility limits expressed as atomic-% of lithium are: 28·3% at 350°C.; 27·8% at 450°C.; 26·7% at 550°C.; 25·3% at 575°C. and 24·1% at 588°C.[36] Freeth and Raynor have confirmed that there is a maximum on the beta-liquidus, 29·0 to 29·4 atomic-% of lithium at 594°C., and the invariant reaction involving the magnesium-rich solid solution, the alpha-phase with the beta-phase and the liquid is a eutectic reaction at 588°C. A detailed study of the form of the alpha + beta/beta boundary shows that although the boundary is almost vertical from 100°C., 29·9 atomic-% of lithium, to 500°C., 29·0 atomic-% of lithium, it bends sharply towards lower lithium contents above 500°C. and intersects the eutectic horizontal, liquid ⇌ alpha + beta at 24·5 atomic-% of lithium.[37] The structure of magnesium–lithium beta-phase alloys has been investigated by Berry and Raynor.[38] A plot of lattice spacing versus lithium content indicates that the (alpha + beta)/beta boundary at 200°C. lies at 30·3 at.-% Li. An alloy containing 34 at.-% Li shows the presence of both the beta phase and a cubic structure of unit-cell 9·7kx. The systematic absences and the relative line intensities in the diffraction patterns can be accounted for by a structure with 32 atoms per unit cell. The lattice spacing is nearly equal to $2\sqrt{2}a$ where a is the lattice spacing of the body-centered cubic beta structure.

Lithium-magnesium alloys tarnish rapidly at room temperature but remain silvery almost indefinitely when immersed in liquid nitrogen. Solid solutions of magnesium in lithium are partially transformed at low temperatures; a phase identified as face-centred cubic is produced in some of the solid solutions of magnesium in lithium during cold work at low temperatures. This phase has a density almost the same as that of the usual form and a unit cell dimension of 4·40 A.; it forms with audible clicks during cold working at a temperature below a critical temperature *Ms*, and increases in amount with increasing deformation at any temperature below *Ms*. The polycrystalline metal is hardened by transformation on cooling and softened by annealing in the neighbourhood of the reversion temperature, Ac, to the body-centred cubic structure. *X*-Ray diffraction tests give a value of 130° ± 10°K. for the transformation temperature of an alloy containing 12 atomic-% of lithium; the reversion temperature is 15° to 30° higher. The highest magnesium content at which appreciable transformation occurs on cold working is about 25 atomic-%

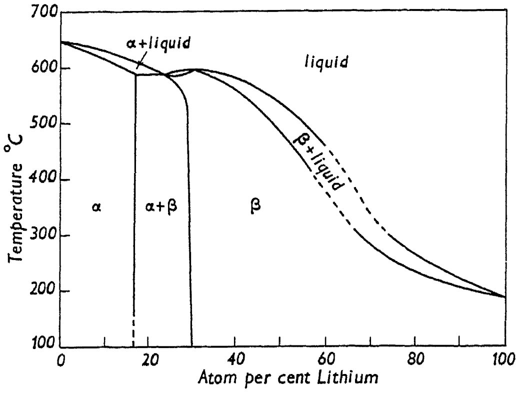

FIG. 4. EQUILIBRIUM DIAGRAM OF THE LITHIUM-MAGNESIUM SYSTEM.[37]

and on simple cooling about 16 atomic-%.[39] The transformation characteristics of a lithium–magnesium alloy containing 12·4 at.-% of magnesium have been further investigated by Barrett and Clifton. In fully annealed fine-grained specimens the critical temperature, *Ms*, which is near 125°K., is slightly lower after annealing near 200°K. than at 300°K. Tests for possible stabilization of the body-centered-cubic phase by annealing in the range of 110°–155°K. during an interrupted cooling experiment discloses no stabilization greater than the estimated error of the best individual experiments. No stabilization of the low temperature phase, hexagonal close-packed structure, is found after annealing at 145°–173°K. during interrupted heating experiments. After cooling below the critical temperature, *Ms*, reversion to the body-centred cubic phase begins slowly as soon as the temperature begins to rise, but rapid reversion begins only when a temperature, *Mr*, is reached which is always higher than *Ms*. The temperature *Mr* and the entire reversion curve above *Mr* shifts to higher temperatures as the previous minimum temperature is decreased. When reversion is interrupted and the specimen again cooled, decomposition of the body-centred cubic phase begins at a temperature, *Ms'*, which is a few degrees above *Ms* and is higher the greater is the % of hexagonal close-packed phase in the specimen.[40]

The density at room temperature, the specific resistance, P_{oo}, at 0°C. and atmospheric pressure, the temperature coefficient of resistance measured between room temperature and 0°C. and expressed as fractional changes of resistance per degree in terms of resistance at 0°C. as unity, of lithium-magnesium alloys are given by Bridgman. (See Table III). The effects of pressure up to 100,000 kg./sq.cm. on the electrical resistance, up to 40,000 kg./sq.cm. on volume compression and up to 80,000 and sometimes 100,000 kg./sq.cm. on the plastic shearing strength, all properties determined at room temperature, are also given. The densities vary almost linearly with composition for alloys containing 100, 99·5, 99·0, 80·0, 60·0, 40·0, 20·0, 10·0, 5·0 and 0 at.-% of lithium. The temperature coefficients drop markedly below the values for the pure metals. Specific resistances plotted against composition show the expected catenary shape for solutions as contrasted with a linear relationship for mixtures. Solubility limits at room temperature are little affected by pressure and there is a general absence of hysteresis or seasoning effects on the initial application of pressure.

Electrical resistance measurements and volume compressions are also given. An alloy, Li(80), Mg(20 at.-%), appears to undergo a polymorphic transition under the action of shearing stress at high pressures.[41]

TABLE III.- DENSITY, SPECIFIC RESISTANCE, AND TEMPERATURE-COEFFICIENT OF RESISTANCE OF LITHIUM-MAGNESIUM ALLOYS

At.-% Li	At.-% Mg	Density	$\rho_{oo} \times 10^6$	Temperature Coefficient $\times 10^2$
100·0	0	0·536	9·17	0·445
99·5	0·5	0·564	11·9	0·438
99·0	1·0	0·536	10·0	0·437
98·0	2·0	0·538	10·1	0·427
80·0	20·0	0·803	24·0	0·136
60·0	40·0	1·070	23·0	0·161
40·0	60·0	1·335	16·0	0·250
20·0	80·0	1·488	11·9	0·252
10·0	90·0	1·644	11·0	0·188
5·0	95·0	1·699	5·56	0·327
0	100·0	1·74	4·17	0·420

According to Linde's rule,[42] $\Delta\rho/A = a\Delta Z^2 + b$ where $\Delta\rho/A$ is the increase in specific resistivity per atomic-% of solute, ΔZ is the difference in valence between solute and solvent atoms, and a and b are constants. This rule does not apply to solutions of metals in magnesium in concentrations of 0–4·4 at.-%. The specific resistivity of magnesium due to alloying increases linearly with alloying content and the ratio $\Delta\rho/A$ is lowest for solutes from Column 1 of the Periodic Table and highest for solutes from Column 4. The increase in specific resistivity per atomic-% of solute depends more significantly upon the Column of the Periodic Table to which the alloying element belongs than upon the period or row. Thus the same value of $\Delta\rho/A$ is obtained for lithium and silver additives, $0{\cdot}75 \times 10^{-6}$ ohm cm./at.-% and a similar value for cadmium.[43] The properties of magnesium–lithium alloys including their density, diamond pyramid hardness, tensile strength, plasticity, and strain-hardening, have been reviewed.[44] Lithium can be added to magnesium-base alloys in amounts up to 12% to improve the creep resistance at elevated temperatures.[45] The production of lithium–magnesium alloys by the electrolysis of molten lithium chloride using magnesium cathodes has been described.[46] Lithium-magnesium alloys containing 52–70% of magnesium may be used as electrodes for electrical systems; they have electropositive properties very close to those of lithium but are far less reactive with water.[47] By the addition of 0·05% of lithium, the ultimate tensile strength of commercial magnesium is increased from 30,000 to 40,000 lb. per square inch and the hardness and corrosion resistance are also increased, but the ductility is slightly reduced.[18] The properties of some magnesium–lithium alloys containing aluminium and zinc,[48] the effect of sodium contamination on these alloys[49] and the ageing characteristics of magnesium–lithium base alloys[50] have been discussed. Corrosion-resistant magnesium alloys containing 1·6% of manganese are improved by adding 2·0–2·75% of lithium. The mechanical properties are: tensile strength 12·35–11·0 tons/sq.in., elongation 14·5–22·5% in 2 in.; a reduction of 45·6% can take place at room temperature.[51] A cast, extruded and heat-treated magnesium-base alloy, composed of 6–12% of lithium, 16–25% of zinc, 1–20% of cadmium and the rest magnesium, exhibits high yield strength under compression loads.[52] Age-hardening of a magnesium–lithium alloy containing magnesium and lithium in the ratio of 5:1 to 10:1 and at least one of the metals zinc, 4–10%, cadmium 4–24%, silver 0–12%, aluminium 4–12%, and having a new crystal phase (θ, a face-centred cubic structure of lattice constant of 6·5–6·92 A.) involves heating at 400°–600° F. to dissolve the θ phase, quenching and reheating at 150°–300° F. to precipitate the θ phase.[53] The addition of lithium to magnesium–cerium alloys has little influence on creep behaviour.[54] The cladding of magnesium–lithium alloys with stainless steel, aluminium or other metals or alloys to produce an article with the high strength of the base alloy and corrosion resistance of the cladding metal is described by Jackson[55] and Frost.[56] Magnesium–lithium alloys containing 30–45% of lithium have an electrical conductivity, on a weight basis, at least 50% of that of copper, and a very low temperature coefficient of electrical resistance $\leq$ 10% that of copper. These alloys when coated with pure magnesium, to prevent atmospheric oxidation, may be used for electrical conductors. Redistilled magnesium, 60 lb., and high-grade lithium of low sodium content, 40 lb., are melted together in an iron crucible in a purified helium atmosphere. The resulting alloy is stirred thoroughly at 900°C., cooled to 750° and cast in a water-cooled iron mould in helium. The ingots are formed into strips and split into electric conductors for use in transformers. The strips are cleaned by mechanical abrasion under light oil, dipped in an N. solution of ethyl magnesium bromide in ether for 10 min., removed and washed with ether. The strips are then coated with pure magnesium of a thickness of about 0·0002 in.[57] A melting flux for magnesium–lithium alloys, which permits good separation of the flux from the metal during pouring, contains lithium bromide which increases the specific gravity of the flux. The following fluxes have been used: 3 parts of lithium bromide, and 1 part of lithium chloride, plus about 10% lithium fluoride, or 75% of lithium bromide and 25% of lithium chloride.[58] Lithium in magnesium–lithium alloys containing 12–13% Li may be determined to within 0·06% of the true value by internal-standard flame photometry.[59] It may also be determined by precipitation in saturated aqueous lithium chloride solution in the form of $LiNi(UO_2)_3,(C_2H_3O_2)_9,nH_2O$. The presence of Mg^{++}, Al^{+++}, Zn^{++}, if less than 10 mg., does not interfere with the determination of 0·1–1 mg. of lithium.[60] Determination of hydrogen in magnesium–lithium alloys is carried out by dissolving the sample in molten tin at 450°C., heating in a borosilicate tube, and measuring the volume of gas evolved. The sample must be protected from air while it is being weighed and loaded into the furnace.[61] Lithium, added to a magnesium base alloy, provides a sacrificial anode *i.e.* one which is more anodic than the normal cell anode, pure magnesium. The two are coupled together electrically and the cell anode becomes cathodic to the sacrificial anode; reactions which normally ensue on storage between the normal anode and the electrolyte are transferred to the sacrificial anode which becomes corroded. The shelf life of such cells is thus increased.[62]

The equilibrium diagram for calcium–lithium alloys has been described; the metals are completely miscible in the liquid state and on cooling a peritectic reaction occurs at 225°C. resulting in the formation of the compound Ca_2Li. This substance forms a eutectic with lithium which melts at 165°C.[63] The compound Li_2Ca has been prepared by melting the theoretical amounts of the metals in argon. Its structure is of the $MgZn_2$ type; the lattice constants are:[64] a 6·248 ± 0·008 A., c 10·23 ± 0·002 A. A process of electrolytic production of lithium–calcium alloys is described in which the anode is placed in the lower portion of a fused bath of lithium chloride and calcium chloride and the cathode in the upper portion of the bath.[65] Lithium–calcium alloys are used for purifying molten metals such as iron or steel,[66,67] copper or copper alloys[68] and nickel or its alloys.[69]

Lithium–calcium alloys when treated with hydrogen under the conditions described below, form solid solutions of the hydrides of lithium and calcium containing 1–50% of lithium hydride and not more than about 3% of calcium and lithium in their elemental forms. These solid solutions are capable of generating hydrogen for use where it would be inconvenient, expensive and sometimes prohibitive to carry hydrogen gas, and are easily shipped. Lithium–calcium

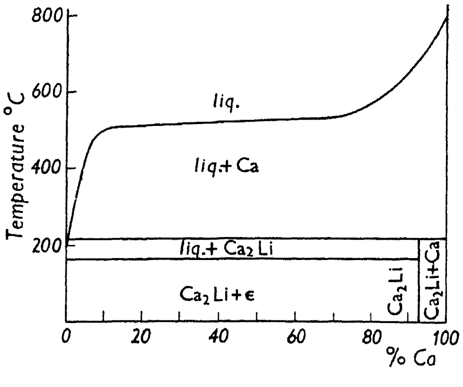

FIG. 5. EQUILIBRIUM DIAGRAM OF THE LITHIUM–CALCIUM SYSTEM.[63]

alloys containing 1, 5, 25 or 50% lithium are used in the form of ingots, 6 in. x 2 in. x 3 in.; they are charged into a reactor which is purged to remove air and gas-heated to about 400°C. Hydrogen is then admitted and the heating supply cut off; the heat of reaction causes the temperature to rise to about 900°C. for the 5% alloy, 1000–1100°C. for the 25% alloy and 1200°C. for the 50% alloy. Hydrogen is continuously supplied to maintain a gauge pressure of about 5 lb. The time of reaction is about 6, 5 and 3 hr. respectively for the 5%, 25% and 50% alloys; after the above times of reaction the hydrogen supply is cut off, the pot is allowed to cool and the product is broken in lumps about 1 in. or smaller. The 25 and 50% alloys yield a distinctly crystalline product. For the 1% alloy, the temperature must be at least 400°C. but not higher than 500°C. and the hydrogen pressure for the first four hours must be at 1 lb. gauge pressure and then raised to 5 lb. This reaction is completed in 12 hr.[70]

Fraenkel and Hahn, in their study of zinc-rich lithium alloys, found that the liquidus temperature decreases from the melting point of zinc to a eutectic point at 0·6% of lithium at 402°C. and then increases to 517°C. at 6% and further to a maximum at 519°C. at 6·2%, corresponding to the formula Li_2Zn_3. Zinc retains about 0·2% of lithium in solid solution and the compound Li_2Zn_3 forms a homogeneous phase with zinc up to a concentration of about 1·4% of lithium.[5,71] Zintl and Brauer prepared an alloy containing 48·7 atomic-% of lithium; it was finely crystalline and on removing the gray outer coating in an inert gas a copper-red surface was exposed. This compound, LiZn, was shown to have the NaTl structure (cf. Sect. XXVI) with a lattice constant 6·209 ± 0·005 A. and density 4·18: the number of atoms per unit cell was 16·3 as compared with 16 for the NaTl structure.[25] The complete phase diagram for the lithium-zinc system has been determined by Grube and Vosskühler and five series of solid solutions are shown, separated by heterogeneous fields. Alloys containing between 1·5 and 5 atomic-% of lithium solidified primarily as alpha-solid solution and a secondary separation then occurred at 403°C. of a eutectic, consisting of alpha- and beta-phases; the eutectic point was at slightly less than 5 atomic-% of lithium and the limits of the eutectic extended from 1·5 to 8·5 atomic-%. Between 8·5 and 20 atomic-%, beta-solid solution was formed directly from the melt. In the concentration range from 20 to 28 atomic-%, gamma-crystals separated out primarily and at 481°C. were transformed to beta-solid solution by a peritectic reaction with the rest of the melt according to the equation: melt + gamma $\rightleftharpoons$ beta. All the alloys containing 24 to 26·5 atomic-% of lithium consisted on complete solidification of beta- and gamma-crystals. The time of arrest of the peritectic reaction could not be calculated because the primary and secondary crystallization temperatures were too close to each other. A further peritectic reaction occurred between 28·5 and 33 atomic-% of lithium: melt + delta $\rightleftharpoons$ gamma. The delta-phase, which separated out directly from the melt between 33 and 50 atomic-%, was characterized by a maximum in the melting curve at 40 atomic-% of lithium at 520°C., and the melt solidified at a constant temperature with the formation of the compound, Li_2Zn_3; between 50 and 98 atomic-%, the molten eutectic crystallized out; from 50 to 95·5 atomic-% the delta-phase separated out primarily and the eutectic secondarily. The epsilon-phase crystallized out primarily between 95·5 and 98 atomic-% of lithium and a eutectic point was observed at 95·5 atomic-% at 161°C. An alloy containing 50 atomic-% of lithium showed a slight arrest at 157°C.; alloys with 98 to 100 atomic-% of lithium solidified to unsaturated epsilon-solid solution. The existence of the compound, Li_2Zn_3, was thus confirmed and a new compound, $LiZn_2$, formed from gamma′ and delta′ solid solutions at 93°C. was detected. The presence of a third compound, LiZn, described by Zintl and Brauer, could not be definitely established although it is probably the delta″-phase. The compound, Li_2Zn_3, which crystallizes out directly from the melt, forms with excess of lithium or zinc the delta-solid solution, and at 174°C. the compound is transformed and forms with the component metals delta′-solid solution on cooling.[5,72] An *X*-ray analysis of alloys prepared by Zintl and Schneider confirms the finding of Grube and Vosskühler that there are five intermediate solid solutions at room temperature. The beta′-phase, with about 10 atomic-% of lithium, has a close-packed hexagonal structure with lattice parameters *a* 2·782 A.; *c* 4·385 A.; *c*/*a*, 1·576. For the gamma′-phase, with about 28 atomic-% of lithium, the lattice parameters are: *a* 4·362; *c* 2·510 A., and *c*/*a* 0·575.[73] The constitution of the delta″-phase, LiZn, has already been described.[25] The binary eutectic of zinc with lithium has been found to be at 403·25°C. and 0·38% of lithium.[74,75] The addition of 0·05% of lithium improves zinc alloys in the same way as does magnesium but, because of the lower equivalent weight of lithium, a smaller amount is required. The presence of lithium in zinc appears to shorten the time required in galvanizing processes.[18] The effect of adding lithium to zinc alloys for constructional materials has been discussed.[76,78] Impurities in zinc, such as lead, tin and cadmium may be removed by the addition of lithium at temperatures between 540° and 60°C. to the molten zinc or zinc alloy. The lithium forms intermetallic compounds with the impurities, Li_7Pb_2, m.p. 726°C., Li_7Sn_2, m.p. 785°C., LiCd, m.p. 549°C. The compound formed with zinc is Li_2Zn_3, m.p. 520°C. The lithium is stirred in at a temperature above the melting points of the intermetallic compounds of the impurities; the temperature is then lowered so that it is above 520°C. and the mixture filtered.[79]

The addition of lithium to zinc–aluminium alloys retards the monotectoid transformation in ageing at room temperature and at 95°C.[80] Other references are given to the addition of lithium to zinc alloys.[81–83]

The oxidation rate of zinc is increased by the addition of lithium.[84]

In their investigation of the lithium–cadmium system of alloys containing 0–30% of lithium, Masing and Tammann suspected the presence of two compounds: $LiCd_2$, at 2·99% of lithium from an observed thermal effect at 356°C., and LiCd at 5·8% of lithium from a maximum setting point at 541°C. As the amounts of material used were small, there is some uncertainty about the temperatures marking the end of solidification.[5] By means of thermal analyses, electrical conductivity and linear expansion measurements, Grube, Vosskühler

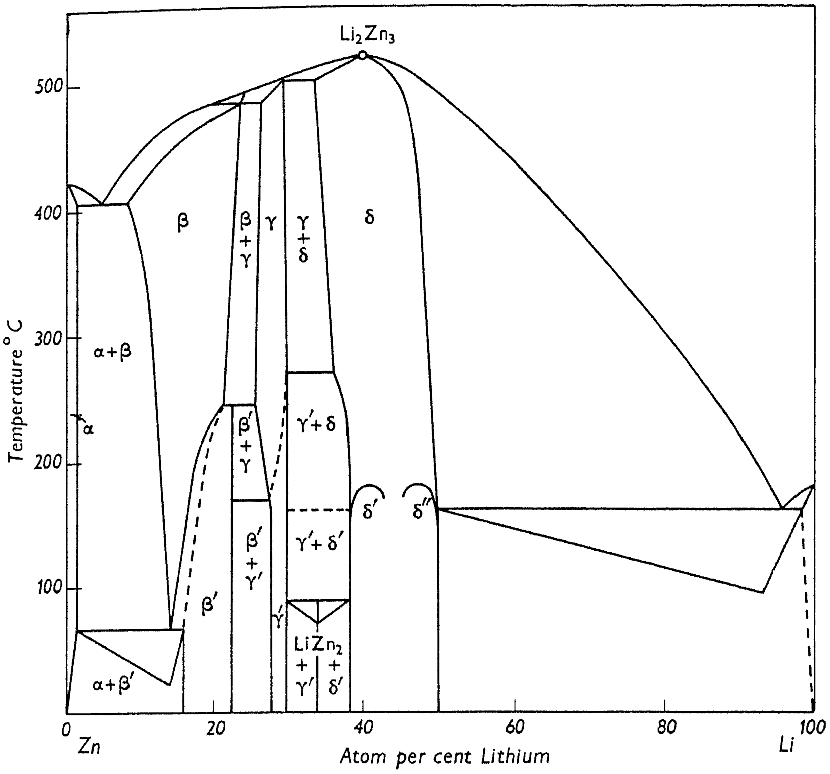

FIG. 6. EQUILIBRIUM DIAGRAM OF THE LITHIUM-ZINC SYSTEM.[72]

and Vogt observed five solid solutions separated by heterogeneous fields. The following compounds were detected: $LiCd_3$ at 2·02% of lithium at 370°C., LiCd at 5·8% and 541°C., and Li_3Cd at 15·63% and 272°C. The primary solid solutions, beta- and gamma-, on cooling to 370°C. and 272°C. were transformed respectively into the compounds $LiCd_3$ and Li_3Cd.[5,85] X-Ray analysis of the above system shows that the compound, LiCd, has a monometric structure of the CsCl type, the unit cell having a 3·32 A.[86] Zintl and Brauer, however, prepared an alloy containing 50·7 atomic-% of lithium, which was finely crystalline and copper-red in colour under its outer coating, and the structure was here shown to be of the NaTl (cf. Sect. XXVI) type with a 6·687 ± 0·003 A., density 5·20, with 15·9 atoms to the unit cell (16 for the NaTl structure).[25] The cubic lattice of the NaTl type for the compound, LiCd, is confirmed by Zintl and Schneider;[87] the lattice has a 4·250 A.[89] Baroni has discussed Zintl and Schneider's results.[88] According to Baroni the compound, $LiCd_3$, is also monometric with unit cell side a 8·62 A.,[86] but Zintl and Schneider give the following parameters: a 3·083 A.; c 4·889 A. and c/a 1·586.[89] The compound, Li_3Cd, found by thermal analysis, could not be identified by Baroni in his X-ray examination,[86] but Zintl and Schneider showed that it has a cubic lattice with a 4·250 A.[87,89] The beta-phase in the lithium-cadmium system exists only at high temperatures and probably has cubic symmetry. The beta'-phase corresponds in composition to the formula $LiCd_3$; the gamma-phase to LiCd and the gamma'-phase to Li_3Cd.[5,89] The modulus of elasticity of the hexagonal phase, $LiCd_3$, is similar to that of cadmium, *i.e.* about 6000 kg. per mm.^{2}; the modulus of elasticity of the cubic face-centred crystal, Li_3Cd, is only slightly higher than that of lithium. Between the phases $LiCd_3$ and Li_3Cd the modulus decreases linearly across the broad field of the LiCd phase.[90]

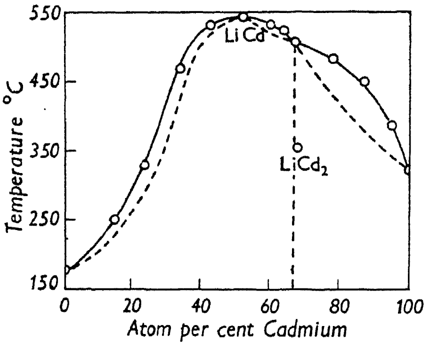

FIG. 7. EQUILIBRIUM DIAGRAM OF THE LITHIUM-CADMIUM SYSTEM.[85]

A phase diagram for lithium-mercury alloys containing 0·1 to 77·4% of lithium has been constructed by Grube and Wolf (see page 112); the existence of the compounds $LiHg_3$, $LiHg_2$, LiHg, Li_3Hg, found by Zukowsky[91] has been confirmed, and two more compounds have been detected, Li_2Hg and Li_6Hg. The compounds LiHg and Li_3Hg melt at 590° and 375°C. respectively; all the other compounds are formed by peritectic reaction and the decomposition temperatures of the following compounds are: $LiHg_3$, 235°C.; $LiHg_2$, 340°C.; Li_2Hg, 375°C. and Li_6Hg, 164°C.[92] Zintl and Brauer prepared an alloy containing 50·9 atomic-% of lithium and showed that this finely crystalline, greyish compound had the same structure as beta-brass with *a* 3·287 ± 0·005 A.[25] Zintl and Schneider have obtained a hexagonal structure for the compound $LiHg_3$ with *a* 6·240 A.; *c* 4·794 A.; *c/a*, 0·768; the unit cell contains 2 atoms of lithium and 6 of mercury. The compound Li_3Hg has a cubic structure with *a* 6·584 A., and there are 4 atoms of mercury and 12 of lithium per unit cell.[93]

The lithium-aluminium system has been studied by many workers. The amount of lithium held in alpha-solid solution has been quoted as 3%,[94] 2·2% at room temperature and 3·5% at 598°C.,[5,95] 3·5% at 590°C.,[5,96] 7 to 8 atomic-% at room temperature[97] and 5·2, 4·44, 3·61, 2·55, 1·87, 1·67 and 0·88% respectively at 600°, 579°, 548°, 501°, 433°, 400° and 223°C.[16,98] The eutectic point between the alpha- and beta-phases has been reported to lie at 590°C. and 7% of lithium,[94] at 598°C. and 7·8%,[95] at 590°C. and 7·3%,[5,96] at 600°C. and 30 atomic-% of lithium[97] and at 602°C. and 26·3 atomic-% of lithium.[99,100] Kipnis and Rogel berg have used the Shreder[101] equation:

$$d \ln \chi / dT = \phi / RT^2$$

to verify the course of the solubility curves of binary metallic systems. Regardless of whether or not the indicated values correspond to the actual values of the heats of solution, it is possible from the nature of the variation of ϕ with T to judge the correctness of the solubility curve, since $\phi = f(T)$.

The relation between the heat of solution and temperature is shown in Fig. 8 for the system aluminium-lithium.[102]

The existence of a compound, LiAl, at 20·46% of lithium with a freezing point at about 720°C. was observed by Müller[5,96] and its presence was confirmed by Grube, Mohr and Breuning[97] and by other workers, who found that it melted

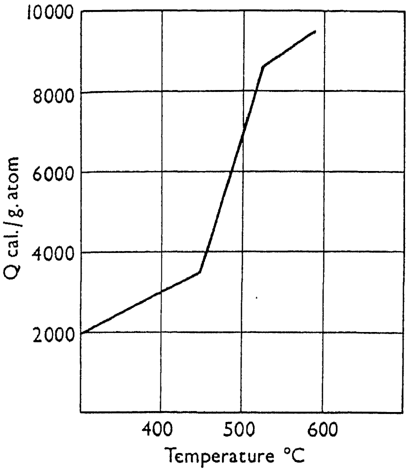

FIG. 8. RELATION BETWEEN HEAT OF SOLUTION AND TEMPERATURE FOR LITHIUM–ALUMINIUM.

congruently without decomposition at 718°C.[99,100] The compound, LiAl, forms with excess of beta-solid solution a homogeneous region which extends at 521°C. from 50 to 56 atomic-% of lithium; the existence of the crystalline compound, Li_2Al, formed at 521°C. by peritectic reaction between beta-solid solution and melt has been observed[97] and its presence was confirmed by later workers at 523°C.[99 100] A hitherto unknown eutectic between the compound Li_2Al (gamma-phase) and lithium (delta-phase) is shown to exist at 94 atomic-% of lithium at 170·6°.[99] An *X*-ray investigation of lithium-aluminium alloys containing up to 20·5% of lithium showed two phases, alpha- and beta-; the alpha-phase displayed no difference in lattice parameters from pure aluminium.[103] Vosskühler, however, found that the addition of lithium to aluminium, in the region of 0·88 to 4·44% of lithium, caused a slight contraction in the lattice, which decreased from 4·040 to 4·037 A. and then remained constant.[98] Others confirm the contraction of the aluminium lattice by solution of lithium and give the following values, measured at 25°C.: pure aluminium, 4·0413 kx; alloys with 0·91, 1·29 and 1·93% of lithium, 4·0396, 4·0392, 4·0381 kx respectively. If the lattice spacing/composition curve is extrapolated to 100% of lithium, the lattice spacing then refers to a hypothetical face-centred cubic modification of the solute, and the corresponding closest distance of approach of the atoms is the apparent atomic diameter of lithium when in solution in aluminium. The apparent atomic diameter is found to be 2·82; the atomic diameter for lithium is 3·03 kx.[104] According to Pastorello, the compound, LiAl, has a lattice constant of 3·23 A., resembling that of the compound LiAg;[24] later workers state that the compound LiAl has a body-centred cubic lattice of the NaTl type with 16 atoms per unit cell, and *a* 6·37 kx[103] or *a* 6·36 A.[105] The radius of both atoms is 1·38 A.[105] The abnormal results of measurements of the irreversible electrode potential of aluminium–lithium alloys (containing up to 13 vol.-% of lithium) in 0·1 N-hydrochloric acid cannot arise from the presence of a protective film and hence must be attributed to a change in the electrochemical behaviour of lithium in solid solution with aluminium.[106] The elastic modulus of aluminium is increased by the addition of lithium in the alpha solid solution region and in the heterogeneous field next to it; for the compound, LiAl, the modulus is greater than would be expected from the law of mixtures.[90] Alloys containing more than 4% of lithium were observed to be readily corroded and those with more than 10% to oxidize rapidly in air and decompose water with

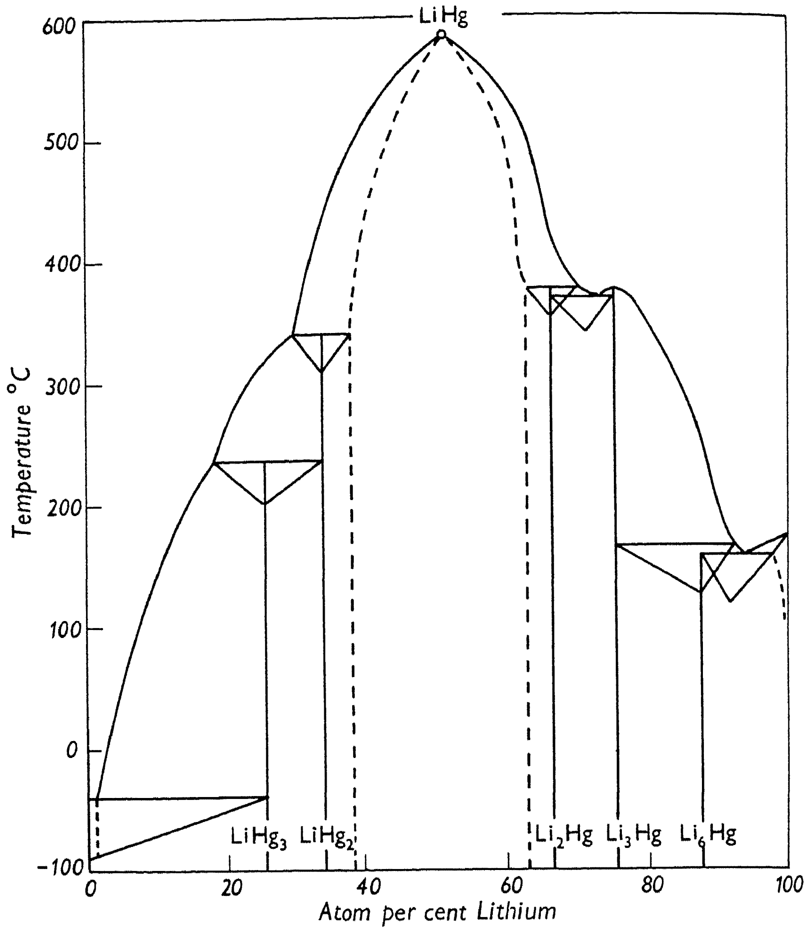

FIG. 9. EQUILIBRIUM DIAGRAM OF THE LITHIUM-MERCURY SYSTEM.[92]

the evolution of hydrogen.[95] It has been stated that alloys containing up to 5·2% of lithium are only slightly corroded after exposure for ten months to 5% sodium chloride solution. The lower resistance to attack found in alloys with larger amounts of lithium is considered to be due to the presence of undissolved $LiAl$.[98] Kroll, however, queries the stability of alloys containing 5·2% of lithium in view of the poor results obtained with alloys of the 'Scleron' type.[107] It has been shown that the aluminium-lithium alloy which exhibits the maximum resistance to corrosion by hydrochloric acid and sodium chloride solutions is one containing 2·94 atomic-% of lithium; a crystalline chemical compound is formed on the surface of such an alloy.[108] The addition of lithium to aluminium increases the Brinell hardness of annealed specimens; the increase is rapid between 2 and 3·5% of lithium and slower above 3·5%. On a weight-% basis lithium produces a greater increase in hardness than does magnesium but on an atomic basis, the reverse is true. The effect of mechanical and heat treatment has also been investigated; annealing cold-worked specimens at 500°C., quenching and ageing at room temperature produced a 16% increase in hardness. Ageing at 100°C. made no appreciable difference while at

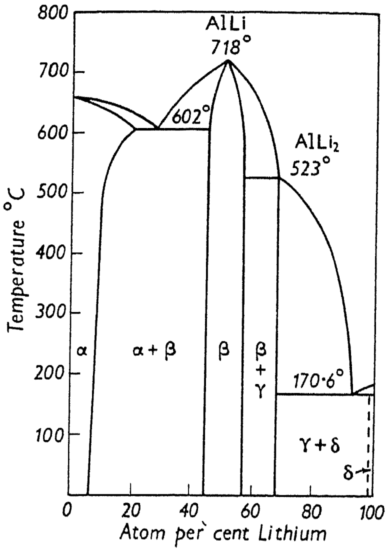

FIG. 10. EQUILIBRIUM DIAGRAM OF THE LITHIUM-ALUMINIUM SYSTEM.[99]

200°C. the beneficial result was lost. A higher Brinell value for the cast than for the worked material was obtained by prolonging the annealing time previous to quenching.[95,98] The importance of silicon in the mechanical improvement of aluminium with lithium has been studied; a 50% increase in hardness was produced when the ratio of lithium to silicon corresponded to the compound Li_3Si; it is suggested that because the solubility of the silicide decreases as the temperature is reduced, the system is converted to a metastable state on quenching and contains the silicide in supersaturated solution. On ageing, the compound Li_3Si separates out in a highly disperse form producing the increased hardness; if ageing is carried out at 200°C. or higher temperatures, the silicide separates out in a coarser form, no longer increasing the hardness.[109] A number of other publications dealing with the improvement of aluminium or its alloys by the addition of lithium are cited.[110-122] Some aluminium-base alloys containing lithium and which can be heat treated, or age-hardened, and possess high strength and other good mechanical properties in conjunction with low density are described. These alloys contain, as cast, 0·2–5% of lithium and not more than, and generally less than, 0·008% of sodium. The deleterious effect of sodium is shown in Table IV, which gives the properties of two alloys, chill-cast under identical conditions, both containing additions of 3·5% of different grades of lithium.

TABLE IV.- EFFECT OF SODIUM ON MECHANICAL PROPERTIES OF ALUMINIUM-BASE LITHIUM ALLOYS

Nature of Li	Na Content by Analysis	Ultimate Tensile Strength Tons/sq.in.	Elongation %
A. Low Na content < 0·02%	0·004%	17·0	0·5
B. Na content approx. 0·35%	0·01%	8·4	Nil

A less obvious effect of sodium when present in amounts which may not affect the properties of the alloy 'as cast' or 'as wrought', is the interference with the response to heat treatment. The alloy is liable to crack during quenching or an embrittling effect is produced.(see Table V).

TABLE V.- EFFECT OF HEAT-TREATMENT ON ALUMINIUM-BASE ALLOYS CONTAINING LITHIUM AND SODIUM

Alloy prepared from:	Analysis Li % Na %	Mechanical Properties					
		As Chill-Cast		Heat Treated(*a*)		Heat Treated(*b*)	
		U.T.S. T/sq.in.	Elong. %	U.T.S. T/sq.in.	Elong. %	U.T.S. T/sq.in.	Elong. %
C. High purity materials	3·69 0·004	15·0	Nil	18·2	0·5	-	-
D. Less pure materials	3·14 0·006	15·25	Nil	Cracked & fell to pieces during machining		11·2	Nil

Heat treatment (*a*) 24 hr. at 510°C., water quenched (cold), 48 hr. at 175°C.
Heat treatment (*b*) 24 hr. at 510°C., water quenched (hot), 48 hr. at 175°C.

The limit of sodium in a heat-treatable, chill cast alloy containing an addition of 3·5% of lithium is 0·005% of sodium, but 0·003% is recommended. The aluminium itself has a sodium content of 0·003–0·005% and may contribute sufficient sodium to make the alloy unsuitable for some purposes.

Ordinary grade lithium contains about 0·35% of sodium; lithium containing less than 0·02% can generally be used with good results.

If both metals contain too much sodium they may be melted directly together under a flux capable of removing sodium. Halides can be used singly or together for this purpose but to avoid removal of lithium from the melt, and contamination of the metals, it is necessary that halides reducible by lithium such as sodium chloride or magnesium chloride should be present in only a small proportion of the mixed flux, or better still, excluded altogether. Good results have been obtained by the use of refined lithium chloride as a melting flux, and where a lower melting point is desired, a eutectic mixture of lithium chloride and lithium fluoride may be used.

Table VI gives results showing the effect of alloying procedure.

TABLE VI.- TENSILE PROPERTIES OF CHILL-CAST ALLOYS CONTAINING ADDITIONS OF ABOUT 3·2% Li AND 0·15% Ti

Analysis Li % Na %	Alloying Procedure	As Cast		Heat Treated	
		U.T.S T/sq.in.	Elong. %	U.T.S. T/sq.in.	Elong. %
E. 3·18 0·005	99·99% Al + high purity Li melted together with Al-Ti master alloy without flux.	17·0	Nil	Weak & brittle and broke on machining	
F. 3·22 0·004	99·99% Al melted in contact with $MgCl_2$ and cast. Al remelted with high purity Li and Al-Ti master alloy without flux.	17·35	1	22·1	2
G. 3·17 0·003	99·99% Al melted together with high purity Li and Al-Ti master alloy using LiCl flux.	16·95	Nil	19·1	1

Heat treatment: 24 hr. at 510°C., water quenched (cold), 48 hr. at 175°C.

The alloy *E* is insufficiently pure to show good properties when heat treated.

The high-proof stress of an alloy (containing 3·22% Li and 0·004% Na, by analysis) when chill cast and heat treated is noteworthy (see Table VII).

TABLE VII.- MECHANICAL PROPERTIES OF CHILL-CAST ALUMINIUM-BASE LITHIUM ALLOYS

Condition	0·1% Proof Stress T/sq.in.	U.T.S T/sq.in.	Elong. %	Brinell Hardness
Chill Cast	15·35	17·35	1	104
Chill Cast. Heat treated: 24 hr. at 510°C., water quenched, 48 hr. at 175°C.	16·9	22·1	2	112

The properties of two alloys in a forged condition, *i.e.* forged bars of 1 in. diameter are given in Table VIII.

TABLE VIII.- MECHANICAL PROPERTIES OF FORGED ALUMINIUM-BASE LITHIUM ALLOYS

Li Content by Analysis	Mechanical Properties							
	As Forged				Heat Treated			
	0·1% P.S. T/sq.in.	U.T.S. T/sq.in.	Elong. %	B.H. No.	0·1% P.S. T/sq.in.	U.T.S. T/sq.in.	Elong. %	B.H. No.
H 2·7	10·5	16·1	14	72	17·7	23·6	7·0	111
J 4·2	9·5	13·9	9	75	24·5	28·7	4·5	140

H Heat treated: 24 hr. at 520°C., water quenched, 24 hr. at 150°C.
J Heat treated: 24 hr. at 510°C., water quenched, 16 hr. at 200°C.

The results in Table IX refer to binary alloys containing an addition of 4·5% Li, extruded into ⅞ in. diameter rod and in various conditions of heat treatment.

TABLE IX.- MECHANICAL PROPERTIES OF EXTRUDED ALUMINIUM ALLOY CONTAINING 4·5% OF LITHIUM

	As Extruded	Soln. heat treated 24 hr. at 530°C., H_2O quenched	Fully heat treated, 24 hr. at 530°C., H_2O quenched, 48 hr. at 200°C.	Precipitation treatment only, 48 hr. at 175°C.
0·1% P.S. T/sq.in.	9·76	9·15	20·6	17·2
U.T.S. T/sq.in.	18·3	19·7	26·3	20·35
Elongation %	7·0	16·0	3·5	1·0
Brinell Hardness No.	75·8	72·3	122	105

The properties of a variety of cast and wrought aluminium-base alloys containing additions of other elements as well as lithium are also given.[121]

Aluminium alloys containing 0·01–1% of lithium, 13–20% of silicon with or without copper up to 18%, silver up to 10% and/or magnesium up to 5%, the remainder being aluminium, can be tempered and used for making pistons and other machine parts.[122] Among such alloys 'Scleron' is of special interest because its physical properties resemble those of mild steel or brass; its tensile strength, elastic properties and hardness are reported to be superior to those of 'duralumin'. A typical composition of 'Scleron' is: 83, Al; 12, Zn; 2, Cu; 0·5–1, Mn; 0·5, Fe; 0·5, Si; 0·1, Li.[18] The use of lithium to improve metallic surfaces has been described: aluminium–lithium wire containing 6·69% of lithium is heated at 590°C. in a bath containing 75% of sodium dichromate and 25% of potassium dichromate; lithium diffuses out to the surface of the wire producing a homogeneous aluminium–lithium coating, resistant to corrosion.[123] Methods for the introduction of lithium into aluminium or its alloys have been described.[124,125]

The compound with gallium, LiGa, containing 9·05% of lithium, has the same structure as the compound NaTl; the side of the lattice, *a*, is 6·195 ± 0·007 A.[5,25] A lithium–gallium alloy of composition Li_3Ga has been obtained by melting the metals together in argon at 600°.[126]

The complete phase diagram for the lithium–indium system has been constructed and only one compound, LiIn, has been detected. It has a bright steel-blue colour, is very brittle and melts without decomposition at 625°C.[5,17,127,128] This compound has the NaTl structure and the side of the lattice, *a*, is 6·786 ± 0·005 A.[25] Lithium is used to activate indium sulphide phosphors.[129]

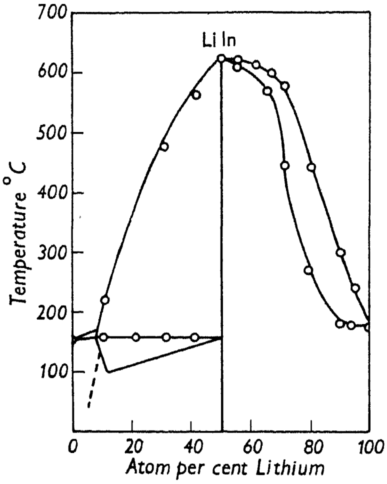

FIG. 11. EQUILIBRIUM DIAGRAM OF THE LITHIUM-INDIUM SYSTEM.[127]

The following intermetallic compounds have been detected in the lithium–thallium system: LiTl, Li_2Tl, Li_5Tl_2, Li_3Tl and Li_4Tl; the last four compounds vary in colour from rose to violet. The compounds LiTl, Li_5Tl_2 and Li_3Tl melt without decomposition; the others decompose on melting and the upper existence limit for both the compounds Li_2Tl and Li_4Tl lies at 381°C. The complete phase diagram has been constructed.[130] Zintl and Brauer have examined the structure of the compound, LiTl, which has a greyish colour, and have shown it to possess the beta-brass structure with a 3·424 ± 0·003 A., and density 8·56, the number of atoms per unit cell being 1·95.[5,25]

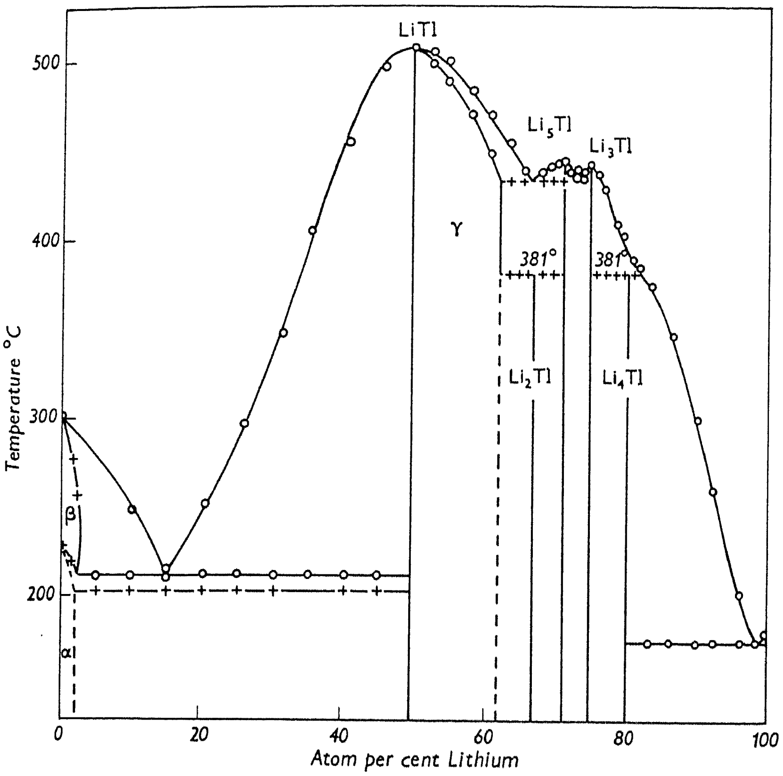

FIG. 12. EQUILIBRIUM DIAGRAM OF THE LITHIUM-THALLIUM SYSTEM.[130]

By thermal analysis and microscopical examination of lithium-tin alloys, Masing and Tammann detected the compounds Li_4Sn, Li_3Sn_2 and Li_2Sn_5 at 81·05, 91·94 and 97·72% of tin respectively. A eutectic point at 175°C. was observed, the eutectic mixture consisting of lithium and Li_4Sn.[4,5] The presence of the compounds Li_4Sn, m.p. 684°C.; Li_3Sn_2, m.p. 483°C., $LiSn_4$ and of three eutectics, m.p. 458°C., 320°C. and 214°C., containing respectively 35, 58 and 94 atomic-% of tin, were observed by Baroni. X-Ray analysis indicated the presence of the first two compounds but the compound $LiSn_4$, which decomposes on cooling, was not identified. The complete phase diagram is given.[131] In their attempt to prepare the compound LiSn, Zintl and Brauer obtained alloys which were not homogeneous.[25] The following intermetallic compounds have been found by Grube and Meyer: $LiSn_2$, upper existence limit 326°C.; LiSn, m.p. 485°C.; Li_2Sn, upper existence limit 502°C.; Li_5Sn_2, upper existence limit 720°C.; Li_7Sn_2, m.p. 783°C.; and Li_4Sn, m.p. 765°C. The compound LiSn forms a solid solution with excess of lithium; the compound Li_7Sn_2 forms alpha-solid solution with excess tin; the compounds LiSn, Li_7Sn_2 and Li_4Sn are formed by peritectic reactions. Pure tin does not hold

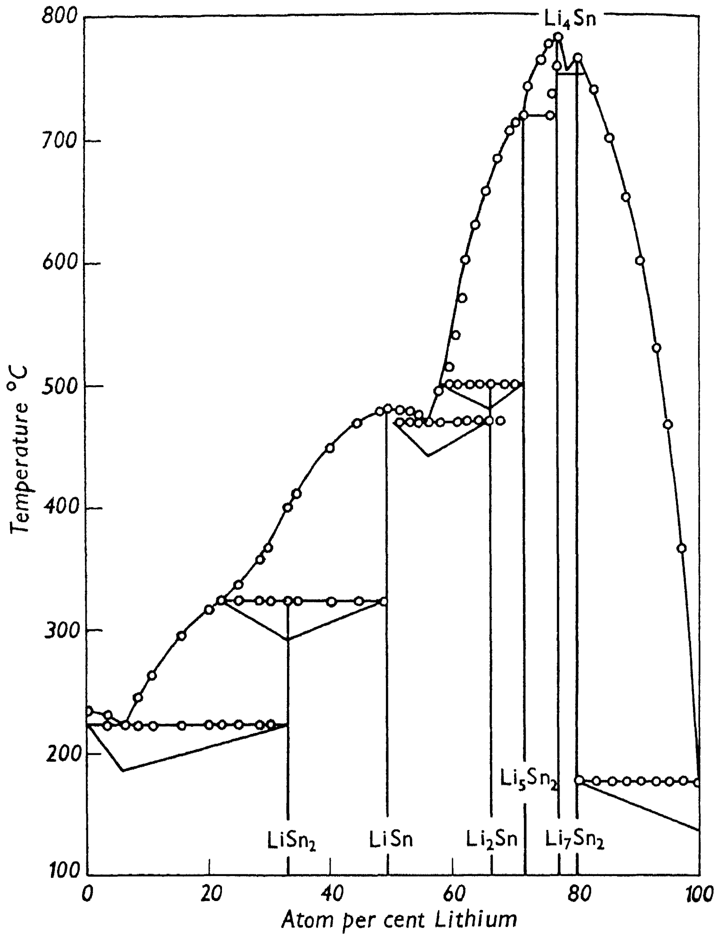

FIG. 13. EQUILIBRIUM DIAGRAM OF THE LITHIUM-TIN SYSTEM.[132]

any appreciable amount of lithium in solid solution;[132] the solid solubility of lithium in tin at 200°C. is less than 0·1 atomic-% of lithium.[133] The average pressure coefficients of electrical resistance up to 12,000 kg. per sq. cm. have been measured at 30°C. and 75°C.;[134,135] selected values are given in Table X.

TABLE X.- PRESSURE COEFFICIENTS OF ELECTRICAL RESISTANCE OF LITHIUM-TIN ALLOYS

Atomic-% Sn	$(1/R_0)(\Delta R/\Delta P)$ 30°	$(1/R_0)(\Delta R/\Delta P)$ 75°
0	$0{\cdot}0_5772$	$0{\cdot}0_5772$
10·0	$0{\cdot}0_58634$	$0{\cdot}0_59046$
40·0	$-0{\cdot}0_56595$	$-0{\cdot}0_56864$
71·4	$-0{\cdot}0_58419$	$-0{\cdot}0_58381$
100	$-0{\cdot}0_59295$	$-0{\cdot}0_59434$

More recently, Bridgman,[41] has examined the effect of pressures up to 30,000 kg./cm.^{2} on the electrical resistance of lithium-tin alloys containing 0–40 at.-% of tin, and included in his specimens Ufford's samples[134,135] which had been kept for 27 years under 'nujol'.

TABLE XI.- LITHIUM–TIN SYSTEM: EFFECT OF TEMPERATURE AND PRESSURE ON ELECTRICAL RESISTIVITY

At % Li At % Sn	100 0	99 1	98 2	95 5	90 10	80 20	60 40
Density		0·552	0·555	0·940	1·50	2·62	
$\rho_{oo} \times 10^6$	9·17	9·02	10·68	15·83	20·66	37·5*	20·9*
Temperature Coefficient $\times 10^2$	0·445	0·437	0·430	0·431	0·428		
Pressure kg./cm.^{2}	*Rp/Ro*						
0	1·000	1·000	1·000	1·000	1·000	1·000*	1·000*
5,000	1·036	1·045	1·036	1·043	1·044	0·945	0·957
10,000	1·074	1·087	1·075	1·091	1·089	0·900	0·921
15,000	1·115	1·130	1·114	1·139	1·137	0·861	0·890
20,000	1·158	1·173	1·176	1·188	1·185	0·829	0·864
25,000	1·198	1·217	1·199	1·236	1·233	0·800	0·840
30,000	1·237	1·260	1·241	1·287	1·278	0·773	0·818

(* Ufford's specimens)

In the above Table densities refer to room temperatures, ρ_{oo} to specific resistance at 0°C. and atmospheric pressure. The temperature coefficient of resistance, measured between room temperature and 0°C., is expressed as the fractional change of resistance per degree in terms of resistance at 0°C. as unity.

The approximate constancy of both temperature coefficient and pressure effect from pure lithium up to 10% of tin, would seem to indicate the very small solubility in pure lithium. Up to 10% of tin the system is almost entirely a mechanical mixture, and if Hansen's diagram is correct this would be a mechanical mixture of pure lithium with the compound Li_4Sn. There would appear to be still another phase not known to Hansen, between 10 and 20 at.-% of tin. The composition 60Li–40Sn corresponds to the compound Li_3Sn_2 shown by Hansen.

The solid solubility of lithium in lead has been given as 0·04 to 0·09%,[136] and 0·03 to 0·1%[18] of lithium. A eutectic is formed at 231°C. and 0·65% of lithium, consisting of the above solid solution and a compound, Pb_3Li_2; beyond this point, the liquidus curve rises to 470°C. at 2·15% where the compound Pb_3Li_2 begins to crystallize out. Alloys containing up to 2·15% of lithium are stable in air; those richer in lithium decompose rapidly.[136] The complete phase diagram has been constructed and the following intermetallic compounds found: LiPb, m.p. 482°C.; Li_7Pb_2, m.p. 726°C. (both of these compounds are formed by peritectic reactions); Li_5Pb_2, upper existence limit, 642°C.; Li_3Pb, upper existence limit, 658°C.; and Li_4Pb, upper existence limit, 648°C. Lead absorbs the compound LiPb in a narrow concentration region with the formation of alpha-solid solution; with excess of lithium, the compound LiPb forms beta-solid solution and the compound Li_7Pb_2 forms gamma-solid solution.[137] According to Rollier and Arreghini, only one compound, $Li_{10}Pb_3$, exists in the region previously shown to contain Li_3Pb, Li_7Pb_2 and Li_4Pb. The compound $Li_{10}Pb_3$ crystallizes in the cubic system with *a* 10·082 kx and has a structure similar to that of gamma-brass.[138] The com-

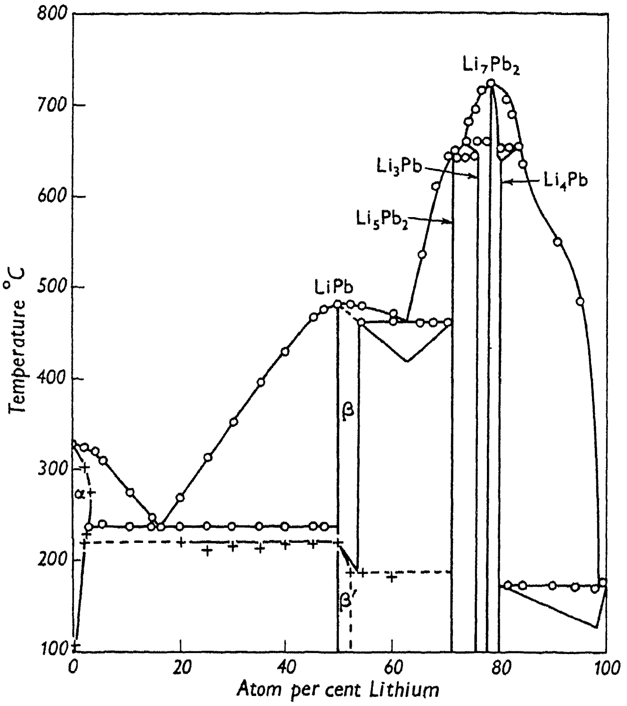

FIG. 14. EQUILIBRIUM DIAGRAM OF THE LITHIUM-LEAD SYSTEM.[137]

pound LiPb exists in two forms with a transition temperature at 214°C. Between 50° and 200°C. the alloy has a negative temperature coefficient of electrical resistance and resistance/temperature curves show an abrupt transition from abnormal to normal behaviour at 186°C. to 214°C., depending upon the composition of the alloy. Above 214°C. the coefficient is positive.[137] Wilson has measured the electrical resistance of an alloy containing 55·6 atomic-% of lithium over a wider range of temperatures and found that at temperatures below 50°C. the alloy behaves as a normal metal. Between 50° and 200°C. the effect described by Grube and Klaiber is observed, resulting in a negative temperature coefficient of resistance; above 200°C. the coefficient becomes positive again. Similar results are obtained at pressures of 5000 kg. per cm.^{2} and 10,000 kg. per cm.^{2}, but the transition temperature is lowered by the increase of pressure. This beta'-beta transformation probably takes place gradually on heating, and a phase of abnormally high energy and entropy content is changed to one of a more normal character. X-Ray methods indicate that the transition is accompanied by movement of the lithium atoms in the lattice to more orderly positions. For an alloy containing 55·6 atomic-% of lithium, the lead atoms are arranged on a body-centred cubic lattice in both the beta'- and beta-phases; the lattice constant is 5·015 A. and the density 6·06. It is suggested that at 0°C. the lithium atoms are more or less irregularly scattered among the many equivalent positions in the lattice, the irregularity giving rise to the abnormally high entropy and the high value of electrical resistance. As room temperature is approached a slight distortion of the lead lattice takes place and the lithium atoms arrange themselves in more ordered positions. The process of distortion and rearrangement continues as the melting point of lithium is approached, culminating in a complete transition to an orderly arrangement at the critical point. The effect of pressure on the beta'-phase is to enhance the distortion and rearrangement process.[139] Nowotny has also examined two alloys near the equiatomic ratio (3·1 and 3·4% of lithium) and found that the beta'-phase, stable at room temperature, is isomorphous with beta-brass and has a lattice constant of 3·522 A. No evidence is found by *X*-ray methods for a disordered high temperature modification, beta-phase, and at 260°C. lines of the beta'-phase are found; the weak interference lines observed are considered to be due to traces of oxide. The *X*-ray density of the beta'-phase is 8·09.[140] The intermetallic compound, LiPb, has been examined also by Gundermann; it crystallizes in a similar way to cæsium chloride and is built up of two simple cubic structures; the author concludes from his results that the compound has a kind of salt-like structure and points out that the radius ratio for Pb^+ and Li^-, 0·74, would be the theoretical value for the cæsium chloride type of structure.[141] Dehlinger and Nowotny have discussed the results of Gundermann.[142] In an application of type models of the electron theory to the crystal chemistry of alloys, the electron arrangements for the lithium-lead system have been tabulated.[143] Alloys consisting mainly of lead are hardened by the addition of about 1 to 3% of lithium; with 1% of lithium a Brinell hardness of 17 is obtained, with 2% a hardness of 25.[144] The addition of 0·07% of lithium increases the hardness of lead to the same extent as does 0·1% of calcium, the resulting hardness in the cast state being 18·5 kg. per mm^2. A diagram has been constructed to show the effect of increase in lithium content from 0·01 to 0·10% on the cast hardness of lead.[145] The tensile strength, modulus of elasticity and hardness of lead are increased by the addition of 0·05% of lithium which produces a fine grain structure and retards crystallization. Lithium has also been used in lead-base, alkali-hardened bearing alloy, *i.e.* 'B'-metal, to which it imparts hardness, especially at elevated temperatures, high resistance to deformation and satisfactory wearing qualities.[18] 'B'-metal, consisting of lithium 0·04, calcium 0·69, sodium 0·62 and aluminium 0·02% with the remainder lead, has been used extensively because of its good frictional properties, but after long service at elevated temperatures some of the hardness is lost as also are some of the alloying metals on melting and casting. Reduction of lithium and sodium to the limit of the alpha-solubility eliminates the loss of hardness for ordinary service temperatures and decreases the loss of alloying elements on melting. Hardness values for a lead-lithium alloy containing 0·04% of lithium, which is slightly in excess of the solid solubility of lithium, and for 'B'-metal are given.[146] Lithium is introduced into lead or lead alloys at a temperature not substantially above 370°C.;[147] it is also used in lead-containing bearing alloys to give sufficiently dense and homogeneous alloys and to effect deoxidation, desulphurizing and outgassing of remelted alloys; means of adding the lithium are described and many references given.[148]

The modulus of elasticity of lead-lithium alloys has been measured from the lead side up to the crystalline compound LiPb; the modulus is first raised by the addition of lithium but decreases in the heterogeneous region. For the compound LiPb the modulus is smaller than would be expected from the rule of mixtures.[90] The density of lithium-lead alloy with 38 at.-% of lithium is 8·19 at 400°C.[149]

Lithium-antimony surfaces are particularly suitable for use in scintillation counters because of their low thermionic emission. The spectral characteristics of lithium-antimony photoelectric cathodes have been determined.[150,151] The addition of lithium to lead-antimony bearing alloys improves their physical properties.[152]

The phase diagram for lithium-bismuth alloys has been determined by thermal analysis and electrical conductivity measurements. The compound, Li_3Bi, m.p. 1145°C., is stable at this temperature; at 415°C. a peritectic reaction occurs with the formation of the compound LiBi, which exists in two forms, alpha and beta, with a transition point at 400°C. No solid solutions are formed. A eutectic between lithium and alpha-LiBi appears at 243°C. and 14 atomic-% of lithium. Between 35 and 37 atomic-% of lithium, beta-LiBi appears only as a primary material. The eutectic, LiBi-Li, appears at 175°C. at 97·5 atomic-% of lithium.[153] The compound, Li_3Bi has a cubic structure with a 6·708 A. and with 16 atoms per unit cell; alpha-LiBi has a tetragonal space-centred structure with a 3·361 A., c 4·247 A. and c/a, 1·264.[5,154] The tetragonal space-centred crystalline compound LiBi has a slightly lower modulus of elasticity than would be expected from the rule of mixtures.[90] Conditions of stability of tetragonal binary lattices are calculated with the help of an interaction energy ϕ of the type, $\phi = (mn\phi_0)\ \{(-1/m)(ro/r)^m + (1/n)(ro/r)^n\}/(n-m)$ where ϕ_0, r_0, m and n are parameters. The dimensions of the unit cell are $r_1 = r_2 \neq r_3$ with $(r_3/r_1) = \gamma$. The interval $\sqrt{1/2} \leq \gamma \leq \sqrt{2}$ is considered. A relation is found between γ^2 and a geometrical parameter α which is identified with the ratio of the radii of the lattice constituents. For LiBr, $\gamma^2 = 1{\cdot}598$ and $\alpha = 0{\cdot}86$. The experimental data are in perfect agreement with the values found on the theoretical curve relating α and γ^2. The Goldschmidt-Bragg model of closed-packed spheres fails in this case.[155]

The alloy, LiBi, prepared from lithium freed from sodium and potassium by partial distillation in a vacuum, is transformed into the superconducting state at 2·4–2·5°K. The alloy $BiLi_3$ is not superconducting.[156] The thorium C isotope of bismuth has been used as an indicator in lithium-bismuth melts and no intermetallic order phenomenon has been noted.[157]

Lithium is insoluble in solid iron; nor does iron dissolve in liquid lithium.[5] When cast iron is treated with lithium the specific gravity of the iron is increased, the tensile strength and hardness are markedly improved and the treated iron can be more easily machined; the graphite in the iron is broken up into small particles uniformly dispersed throughout the metal and in the case of low-carbon grey iron the graphitic carbon is changed to carbide. Examples are given showing the improved properties of the lithium treated iron. A considerable increase in elastic limit is obtained when carbon steels are treated with lithium. The addition of a lithium alloy to stainless steel, 'Nirosta' KA_2, Allegheny metal, improves its fluidity so that it can be poured at a temperature at which the untreated metal is sluggish; the metal shrinks more uniformly instead of showing the 'centre pipe' effect; its tensile strength, Brinell hardness and elongation are increased and the non-metallic impurities are appreciably less and are more finely divided and uniformly distributed within the crystal and not along the grain boundaries. The metal is also freed from gases and its specific gravity increased; the treated steel has a higher resistance to corrosion and better polishing qualities. Other chrome-nickel steels behave in the same way.[18] The use of lithium in the production of nodular iron has been described.[158-167] Roos critically reviews the solidification process of ordinary and nodular cast irons and attributes the formation of spheroidal graphite in the latter to the existence of a dense α-allotrope, the formation of which is enhanced by lithium and magnesium. These elements increase the diffusion rate of carbon.[168]

The elastic limit, tensile strength, elongation and fluidity of nickel and its alloys are improved by treatment with lithium; one of the most harmful impurities in nickel is sulphur for which lithium has a high affinity.[18] The nickel in '304' stainless steel is leached from the surface and grainboundaries when a test piece is exposed to the action of lithium for forty hours at 1000°C. After 400 hours, the removal of nickel occurs to a considerable depth and cavities are visible in photomicrographs of the test specimen; this is a case of selective solution, and as a consequence of the reduced nickel content the face-centred cubic phase (austenitic) is rendered unstable and transformation to the body-centred cubic phase (ferritic) probably occurs.[169] The method of introducing lithium to nickel-rich alloys, such as nickel bronzes, and its effect on their physical properties have been described and many references are given.[148,170] Lithium-nickel alloys are improved by heating to high temperatures, rapidly cooling and subjecting to mechanical working at low temperatures.[171]

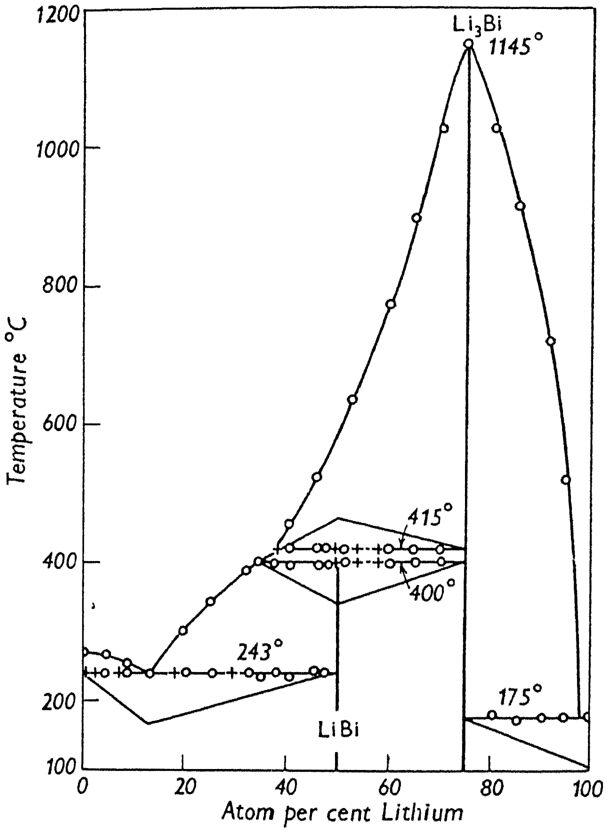

FIG. 15. EQUILIBRIUM DIAGRAM OF THE LITHIUM-BISMUTH SYSTEM.[153,169]

The addition of 0·02–1·0% of lithium to zirconium permits a quiet arc to be struck and maintained at 15–40 V. and 800–1800 amp., depending upon the electrode size. Argon is preferred as an inert atmosphere because it ionizes and assists the volatile metal in maintaining a steady arc.[172]

The tertiary system, magnesium-silver-lithium, has been investigated; the solubility of silver in magnesium is slightly increased by the presence of lithium whereas the solubility of lithium in magnesium is greatly reduced by the presence of silver at 421°C. The region of the alpha-solid solution is very much smaller at 321°C. than at 421°C. and the isothermal at 205°C.

shows how greatly the extent of the primary solid solution has narrowed at this temperature; very little silver can be held in solid solution at 205°C. As much as 13 atomic-% of lithium can be introduced into magnesium-silver alloys without taking the resultant alloy outside the (alpha plus Mg_3Ag) region. Alloys containing 26–30 atomic-% of lithium in the homogeneous beta-phase melt above 580°C. and, having a body-centred cubic structure, offer the possibility of ductile alloys lighter than magnesium. Preliminary experiments on corrosion have shown that alloys consisting of a few atomic-% of silver and up to 20 atomic-% of lithium show no obvious signs of corrosion after exposure to a domestic atmosphere for five months; alloys with 15 atomic-% of lithium with and without the addition of 1 atomic-% of silver or of silver and aluminium are only slightly tarnished on heating at 300°C. for 20 hours; they do not crumble to powder but appreciable quantities of a black powder are formed. These alloys cannot, however, be expected to resist salt-water corrosion.[173] The magnesium-lithium-silver system has been re-investigated more recently by Freeth and Rayner, particularly at the (alpha + beta)/beta phase boundary at temperatures between 208° and 500°C. The ternary beta-phase enters into equilibrium with alpha-phase, Mg_3Ag and MgAg; the lithium-rich corner of the alpha + beta + Mg_3Ag phase triangle occurs at the following composition for the temperatures studied:-

208°C. 4·5 atomic-% of silver; 25·5 atomic-% of lithium
305°C. 10·0 atomic-% of silver; 20·3 atomic-% of lithium
410°C. 14·3 atomic-% of silver; 12·5 atomic-% of lithium

At 495°C., beta-phase and liquid co-exist and experiments at 500°C. indicate that approximately 20 atomic-% of silver dissolves in the beta-phase at this temperature. A wide range of solution of lithium in the MgAg phase is also indicated.[37]

The ternary system, aluminium-magnesium-lithium, has also been studied and it has been shown that only one ternary compound, phase *X*, which has a composition approximating to Al_2MgLi, exists; it decomposes before melting into solid solutions. Ten phases are found in the system, nine being formed by primary crystallization since phase III forms IV in the solid state. Phases I, V and VII are solid solutions based on aluminium, magnesium and lithium respectively. The remaining phases, except *X*, are solid solutions based on binary intermediate phases. There are two ternary eutectics, one consisting of the phases V, VI and X at 419°C. and one involving VI, VII and VIII at less than 170°C. There are six transition points: (1) X + liquid → VI, 472°C.; (2) IX + liquid → X, 498°C.; (3) IV + liquid → X, 422°C.; (4) IX + liquid → X, 434°C.; (5) IX + liquid → VIII; (6) IV + liquid → II. Some of the phases rich in low-melting lithium have high melting temperatures.[174,175] The close-packed hexagonal structure of magnesium is converted to a ductile, malleable body-centred cubic lattice by the addition of lithium in excess of 10%, and the density of magnesium and magnesium-base alloys is decreased by the addition of lithium. The magnesium-rich corner of the 375°, 200° and 100°C. isothermals of the magnesium-aluminium-lithium system has been examined by metallographic and *X*-ray diffraction studies and the following results obtained. The phases in this corner are the magnesium-rich alpha solid solution, the lithium-rich beta solid solution, and the binary compounds $Mg_{17}Al_{12}$ and AlLi. The alpha and beta solid solutions are widely different in etching characteristics. The lithium-rich solid solution is very reactive chemically and even a rinse in ordinary tap water produces a distinctive brown film; the magnesium-rich solid solution remains unattacked. Typical structures of the various alloys are illustrated and *X*-ray diffraction patterns for each of the four phases agree with published data, and with patterns obtained from laboratory melts with synthetic compositions corresponding to the theoretical composition of each phase. Additional lines, usually very faint, are found on occasions and these could be attributed to nitrides or carbonates. Four of the additional lines are more intense and occur frequently but not consistently in alloys containing substantial amounts of beta solid solution. These lines correspond in both angle and intensity to the four principal lines reported for the ternary compound, $MgLi_2Al$. Several alloys of composition approximating to $MgLi_2Al$ have been prepared and diffraction patterns obtained immediately after heat treatment in a purified helium atmosphere at 400°, 375° and 100°C. In all cases the alloys contain the compound AlLi with beta solid solution or with alpha + beta, but there is no trace of the four additional lines. The equilibrium compound, $MgLi_2Al$, does not, therefore, exist in the temperature range 100°–400°C. No evidence of the four additional lines is found in alloys containing 4–15% lithium and 12–30% aluminium after homogenizing treatment at temperatures of 400°, 375° and 100°C. They are only found in the region near the beta corner of the alpha-beta-AlLi and beta-AlLi areas and from specimens homogenized at 375°C. and aged at room temperature or 100°C. for a considerable period. Hence, although the lines cannot be reproduced consistently, even with specimens of the same alloy, it is believed that the four diffraction lines are due to a transitional structure.

For the 375° isothermal section the alpha-beta-AlLi field occupies a large part of the central section whereas the alpha-AlLi-$Mg_{17}Al_{12}$ field is extremely narrow. The solubility of aluminium in magnesium first decreases and then increases slightly until the alpha-$Mg_{17}Al_{12}$ boundary meets the corner of the ternary area for alpha solid solution and the two binary compounds. Above this point the solubility of aluminium again decreases. No additional phases appear in the 200° isothermal section. The alpha, beta, alpha-beta and alpha-$Mg_{17}Al_{12}$ fields, however, retract abruptly towards the binary surfaces, permitting a marked expansion of the four fields containing the compound AlLi. With a further decrease to 100°C., retraction of the alpha, beta, alpha-beta and alpha-$Mg_{17}Al_{12}$ areas continues much more slowly. As the beta solid solution is the most ductile phase, the portion of the equilibrium diagram of greatest interest, from the practical viewpoint of developing alloys combining good workability and strength, adjoins the alpha-beta/alpha-beta-AlLi phase boundary. It is shown that beta and alpha-beta alloys supersaturated with the compound AlLi can be obtained by quenching from a homogenizing temperature in the vicinity of 375°C., and that a massive precipitation of AlLi can be avoided by suitable ageing treatment.[176] The spectrographic character of the luminous trails generated by ultra-high-speed pellets of lithium–magnesium–aluminium has been investigated.[177,178] The properties of magnesium–lithium alloys containing aluminium and zinc and the effect of contamination of such alloys with sodium have been discussed.[35,49,63]

The system aluminium–zinc–lithium has been examined by thermal analysis and a study of the microstructure of the solid alloys. The phases in equilibrium with the alpha-solid solution of aluminium at room temperature are: beta-solid solution of zinc, phases of variable composition, gamma- and delta-, formed by a peritectic reaction, and epsilon-solid solution of the compound AlLi. The limits of alpha-solid solution have been determined at various temperatures.[179] The composition and temperature of the ternary eutectic are 4·31% of aluminium, 0·52% of lithium and the remainder zinc at 364·25°C.[74]

The spectral photoelectric sensitivities of germanium–lithium–silver compounds have been measured.[180]

A new phase has been observed in the lithium–germanium–aluminium system on introducing about 1% of lithium into an aluminium–germanium alloy containing about 65% of germanium; it consists of coarse angular particles in or alongside the primary germanium crystals, and on standing in air the light-grey colour of the new phase darkens and the surface becomes covered with deep cracks; a new phase in the aluminium–silicon–lithium alloys behaves similarly.[181] The following compounds have been prepared by Juza and Schulz[126] by heating together the binary phosphides or arsenides at the temperatures stated in brackets: Li_5GeP_3 (700°–1000°C.); Li_5TiP_3 (800°–900°C.); Li_3GaP_2 (450°–650°C. in the presence of excess lithium phosphide); Li_3GeAs_3 (700°–850°C.); Li_5TiAs_3 (600°–700°C.); Li_3GaAs_2 (450°–650°C.). The reaction is completed in two to three hours.

By thermal analysis, which shows three arrests on the cooling curve, a new ternary phase, $Li_xAl_ySi_z$ has been detected in the aluminium–silicon–lithium system; the new phase appears as light grey to light lilac crystals against a background of a solid solution of silicon in aluminium and of fine dark grey crystals of silicon. The new phase gradually becomes covered with a network of thin cracks.[182] Electrolysis of barium aluminate with cryolite and lithium halide yields no definite compound but an alloy of aluminium, barium and lithium.[183]

The effect of lithium in alloys[184,185] and the use of lithium alloys for purifying metals and alloys[186] have been described. The addition of lithium has little effect on the creep strength of magnesium–cerium alloys at 250°, 300° and 316°C.[187] The addition of lithium to silver–copper alloys nullifies the harmful effects produced by the presence of solid inclusions such as cuprous and cupric oxides.[188]

In making alloys of light and heavy metals, the light metal, such as lithium, is introduced in measured amount into a cavity formed in a relatively dense metal or alloy, the opening is closed and the whole heated until the interior unites with the exterior metal. The metal object thus obtained is added to the principal metal to be alloyed in the fusion bath.[189] A similar device employing a cartridge for below-surface treatment of molten metals is described. A metal container with a cavity filled with lithium is closed with a fusible plug of melting point above that of lithium and below that of the cartridge case. The weight of the cartridge and its charge exceeds the weight of the corresponding volume of molten bath metal into which the cartridge is lowered.[190] An improved tumbler stirring mechanism for the incorporation of additives into molten metal (particularly cast iron) is especially suitable for mixing highly volatile or explosive materials. Lithium or magnesium may be added by means of this device.[191]

An account of lithium and its alloys is given by Shamraĭ.[192]

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SECTION VI

LITHIUM HYDRIDE

By MARY R. TRUTER

At ordinary temperatures lithium hydride is an ionic solid compound of lithium cations and hydrogen anions. It is a very light, white salt which melts at 680°C. and is decomposed by water. In general, liquids that are normally used as solvents for investigating chemical reactions either do not dissolve lithium hydride or they are decomposed by it. Consequently, investigation of its chemistry is severely limited, and those reactions that have been explored are of necessity heterogeneous. This in turn means that it still has no important industrial uses.

Formation, Preparation and Production

It has long been known[1] that lithium hydride is formed by the direct action of molecular hydrogen on molten lithium. Other reactions by which the hydride is formed have been noted more recently. The reaction of atomic hydrogen with the solid metal at room temperature is instantaneous.[2] Lithium hydride is precipitated by the reaction[3] between lithium methyl and triphenyltin hydride in ethereal solution in a stream of nitrogen. The hydride is also formed[4] from lithium methyl by reaction with lithium aluminium hydride: again reaction occurs in ethereal solution and a white precipitate containing 88% of lithium hydride is formed; but this reaction is merely of interest as an illustration of a general method for preparing metallic hydrides, because the lithium aluminium hydride is itself prepared from lithium hydride.

The rate of reaction between lithium and hydrogen or deuterium has been studied by several workers.[5-7] The rate of formation of the deuteride is somewhat greater than that of the hydride.[5] In a recent study of the rate of reaction and the influence of promoters,[7] metallic lithium (0·25g.) in a nickel boat was placed in a 500 c.c. vessel and heated to 500°C. and 525°C. in vacuum. Hydrogen was admitted until the pressure reached 0·5 atm. and the rate of fall in pressure was measured manometrically. Reaction was fairly slow at both temperatures, e.g., at 500° the metal absorbed 118 times its own volume of gas in 30 min. At higher temperatures lithium sublimes at pressures less than atmospheric, and so the normal preparation of the hydride is carried out at increased pressures. In other experiments lithium metal, in hydrogen at 0·5 atm. pressure, was heated from room temperature at the rate of 2–3°C. per min. At first the pressure increased linearly because of thermal expansion, then the rate ceased to be linear because absorption of hydrogen had started (at temperature t_i). Eventually the rate of absorption became greater than the rate of thermal expansion (see Fig. 1) so that the pressure decreased as the temperature increased. Thus, the pressure passes through a maximum at a temperature t_c. Addition of small amounts of other metals, 'promoters', to the lithium generally results in a reduction of t_i and t_c, as shown in Table I.

It is interesting to note that t_c corresponds to the temperature of formation generally quoted in the literature, the early investigations[8] having shown that there was a small uptake of hydrogen at 300° followed by an induction period

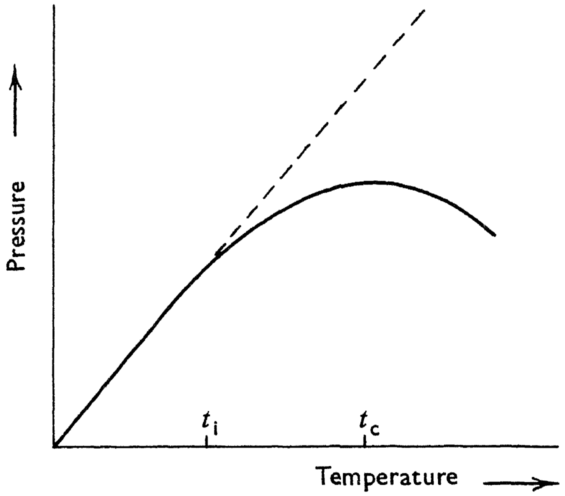

FIG. 1.

TABLE I. - EFFECT OF 'PROMOTERS' ON THE FORMATION OF LITHIUM HYDRIDE[7]

Promoter:	None	5·56% Mn	5·5% Ce	5% Ca	6·65% Ni	7·1% Ni + 4·8% Mn
t_i, °C.:	200	170, 170	160, 175	200, 200	250	150
t_c, °C.:	550	375, 400	490, 490	500, 500	450	450

in which no reaction took place, then a very vigorous reaction set in at 500-520° and was complete in 10 min. Soliman[7] showed that the absorption at temperatures below 500° was due to reaction and not to solution because no hydrogen was given off on cooling.

The earliest method for preparing lithium hydride is still the only practical one, and in 1950 details for the preparation of over a kilogram of very pure hydride were given.[9] The metal (890g.) was quickly placed in a reaction vessel which could be evacuated and was contained in a furnace. After the apparatus had been evacuated, hydrogen was admitted and allowed to flow slowly through at a positive pressure of about 0·25 atm. During an hour the furnace was heated to 500°C., at which temperature the reaction became perceptible. The temperature was raised to 650° and then kept approximately constant below 700° (the m.p. of the hydride is 680°). The lithium hydride formed is completely soluble in lithium. After about three hours, when no further absorption of hydrogen was detectable, the vessel was kept at 690° for 20-30 min. and then allowed to cool slowly, during two hours, to 300°, after which it was cooled more rapidly. The yield was 98·5% of the theoretical, and the product had a purity of 99·6%. Some preparations are white and some have a faint blue tint, but they are not distinguishable chemically. This method has been used by later workers, some of whom have suggested minor improvements in the apparatus.[10]

Commercial production of lithium hydride is also based on the reaction of hydrogen with molten lithium. Patents deal either with methods for producing the metal from its compounds[11-14] or with methods for increasing the rate of reaction (so that a lower temperature can be used) by increasing the surface area of the metal.[15-17]

To increase its surface area, the molten metal is mixed[15] with finely divided sodium hydride and 0·1–1·0% of a salt of a fatty acid or a hydrocarbon containing more than eight carbon atoms per molecule; the temperature required for the reaction is about 450°C. Alternatively, molten lithium, a metallic hydride and sand or clay are mixed and allowed to react, at about 385°C., with hydrogen containing 0·05–1% of an acetylenic hydrocarbon.[16] In another method the molten metal, dispersed in an inert hydrocarbon oil, is allowed to react at about 450°C. with hydrogen under a pressure of about 33 atmospheres.[17]

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Physical Properties

Lithium hydride is the simplest of all known stable compounds and the second simplest diatomic molecule, consisting of two nuclei and four electrons. It is inevitable, therefore, that it should have been the subject of considerable calculation, many theoretical approaches having been tested by their ability to predict the physical properties of lithium hydride. The two extreme postulates for the bonding are (a) that there is an electron-pair bond and (b) that there is complete ionization into two helium-type ions Li^+ and H^- both in the solid and in the gas, the latter consisting of ion pairs. Some of the physical properties have been calculated although they have not yet been measured, e.g., the dipole moment, and attempts have been made to derive values[1,2] for unmeasurable properties, e.g., the normal potential for the hydride ion.

Melting Point, Density and Crystal Structure.

Lithium hydride is usually a white crystalline solid at room temperature; the hydride melts at 680°C.[3] and the deuteride at 686 ± 5°C.[4] Early workers[5] observed that the solid changed colour in daylight, becoming pink or brown. In ultra-violet light it becomes blue and the colour can be discharged by heating the solid; this behaviour is similar to that of the alkali halides and was one of the observations that led Moers[5] and Nernst[6] to postulate that the compound was a salt analogous to lithium fluoride. Moers's classical work[5] also showed that the crystals are isotropic, like those of the lithium halides, and that the solid can be electrolyzed to give hydrogen at the anode and metallic lithium at the cathode. The analogy with the halides of lithium was more apparent when the crystal structure was found[7] to be of the rock-salt type like the lithium halides.

From *X*-ray diffraction photographs the axis length, *a*, of the cubic unit cell has been determined. Values of *a* are shown in Table II together with the calculated density and molecular volume. The density, and hence the molecular volume, have also been determined pyknometrically. Here, the main difficulty arises from the necessity for absolutely anhydrous conditions. The results and comparable predicted values are also shown in Table II. It is interesting to note the contraction in the lattice when hydrogen is replaced by deuterium.

TABLE II. - DENSITY, MOLECULAR VOLUME AND UNIT CELL DIMENSIONS OF LITHIUM HYDRIDE

Workers	Date	Method	*a* (*kX*.)	Density (g./c.c.)	Molecular volume (c.c.)
Moers[5]	1920	Pyknometer	-	0·816	9·77
Fajans and Grimm[8]	1920	Prediction (room temperature)	-	-	11·46
Bijvoet and Karssen[7]	1922	*X*-Ray	4·10	0·76	10·45
Bijvoet[9]	1923	*X*-Ray	4·10	0·76 ± 0·01	10·45
Hüttig and Krajewski[10]	1924	Prediction (absolute zero)	-	-	9·8
Proskurnin and Kazarnovskii[11]	1928	Contraction of Li lattice	-	-	9·8
Bode[12]	1931	Pyknometer	-	0·705 ± 0·02	11·29
Zintl and Harder[13]	1931	*X*-Ray	4·084	0·77	10·32
Idem.[14]	1935	*X*-Ray LiH LiD	4·085 ± 0·001 4·065 ± 0·001	0·774	10·33 10·18
Tronstad and Wergeland[4]	1938	*X*-Ray LiH LiD	4·085 ± 0·001 4·063 ± 0·001	0·878 ± 0·002	-

The intensities of the *X*-ray reflexions have been measured by three independent groups of workers, from powder[13,16] and from single-crystal[17] specimens, and all three sets of results have been shown[18] to be in good agreement, so that there is no doubt about the accuracy of the experimental data. All these investigations have shown that the atoms or ions are arranged in a rock-salt (NaCl) lattice, so that the measured intensities of the reflexions should depend only upon the scattering powers (scattering factors[15]) of the atoms or ions, and these in turn depend upon the electron-density distributions. Thus it appears that measurement of the intensities might show whether the crystal contains the ions Li^+ and H^-, each with two electrons, or the atoms Li (with three electrons) and H (with one electron), the number of electrons being equal to the scattering factor at $\sin\theta = 0$. Further, the observed electron-density distribution could be compared with that calculated from various theoretical models. Attempts to deduce the charges on the ions have led to values ranging from[13] 1 to 0·25.[17] Recently it has been shown that the scattering factors for H and H^- are nearly the same,[18] and independently that the scattering factors from models with charges of unity or zero are nearly the same[19] at observable values of sin θ, so that the extrapolation to sin $\theta = 0$ is not likely to give a significant result. Theoretical treatments have also indicated quite different charges, 0·35 in[20] 1936 and nearly 1 (corresponding with an ionic structure with some overlap) in 1953.[19]

The coefficient of thermal expansion has not been measured, but has been calculated[21] to be $3{\cdot}9 \times 10^{-5}$ per degree for lithium hydride, $5{\cdot}7 \times 10^{-5}$ per degree for lithium deuteride and, for the still unknown lithium tritide, $6{\cdot}3 \times 10^{-5}$ per degree. From measurements[22] of the intensities of the lines on the X-ray powder diagram from 20°K. to room temperature, the Debye characteristic temperature[23] was calculated to be 851°K. for lithium hydride and 638°K. for lithium deuteride.

The refractive index of the crystals is $n_D = 1{\cdot}615$, corresponding to a molar refraction of 3·94 for lithium hydride.[12]

Lattice Energy and Specific Heat.

Values for the ionic lattice energy, U_0, calculated from the Born cycle and from spectroscopic data, have been compared with those predicted theoretically; unit-cell dimensions have also been predicted. The quantities required for the Born cycle and the assumptions made in the determination of the lattice energy from the absorption spectrum of the solid are shown below.

$$\begin{tikzcd}
\mathrm{Li^+H^-(s)} \arrow[r, "U_0"] \arrow[dr, "h\nu"] & \mathrm{Li^+(}g\mathrm{)} + \mathrm{H^-(}g\mathrm{)} \arrow[d, "E-I"] \\
\mathrm{Li(s)} + \tfrac{1}{2}\mathrm{H_2(}g\mathrm{)} \arrow[u, "-\Delta H_f"] & \mathrm{Li(}g\mathrm{)} + \mathrm{H(}g\mathrm{)} \arrow[l, "S + \frac{1}{2}D(\mathrm{H_2})"']
\end{tikzcd}$$

Thus, $U_0 = I - E + S + \tfrac{1}{2}D_{(\mathrm{H_2})} - \Delta H_f$, where I is the work of ionization for lithium, E is the electron affinity of hydrogen, S is the heat of sublimation of lithium, D is the dissociation energy of hydrogen and ΔH_f is the heat of formation of lithium hydride. It was assumed[35] that the absorption spectrum of the solid arises from an electron transfer within the lattice. There is a sharp maximum at 2517 ± 2A. in the absorption spectrum of lithium hydride[35,37] and at 2482 ± 5A. for lithium deuteride.[35] From these observations the values of the lattice energies in Table III were derived,[35] the value of E being taken as 16·4 kg.-cal. per g.-mol. In a critical evaluation of all the previous theoretical work on the solid, Lindqvist[26,27] points out that a completely ionic model is not as acceptable for the hydride as for the alkali halides because the hydride

TABLE III.- CALCULATED UNIT-CELL DIMENSIONS AND LATTICE ENERGIES OF LITHIUM HYDRIDE

Workers	Date	*a*, calc.	U_0(kg.-cal./g.-mol.)	
			Predicted	Born cycle
Kazarnovskii[1]	1928	–	234	234
Bradley[2]	1929	4·36A.	230·5	245·2
Kazarnovskii[24]	1930	–	–	217 ± 7
Hylleras[25]	1930	4·42A.	219	217
Kapustinskii, Shamovskii and Bayushkina[35].	1937	–	From the absorption spectrum, 219·2(LiH) 220·8(LiD)	
Lindqvist[26]	1954	–	205	–

ion is more easily deformed. A summary of the results of calculation by wave or quantum mechanics and from experimental data is given in Table III.

The zero-point energy has been calculated in a number of ways; from the more rigorous London formula it is 1·12 kg.-cal. per g.-mol. for lithium hydride and 0·59 kg.-cal. per g.-mol. for lithium deuteride,[28] whereas for one approximation values of 5·49 and 4·30 kg.-cal. per g.-mol., respectively, are obtained,[28] and for another approximation 3·69 and 2·77 kg.-cal. per g.-mol. respectively.[4] Values deduced from spectroscopic data are 1·9797 and 1·4878 kg.-cal. per g.-mol. for lithium hydride and lithium deuteride, respectively.[4] Although the actual values depend upon the theory invoked, there is agreement that the zero-point energy for the deuteride is less than that for the hydride, in harmony with the suggestion[29] that the observed contraction in the lattice is due to the difference in zero-point energy. The calculated contraction,[29] however, is only half that observed.[14]

The molar specific heat of the solid calculated from Debye's formula[30] is in good agreement with that measured[31] over a range of temperatures from 74°K. to room temperature; the values are shown in Table IV.

TABLE IV. - THE MOLAR SPECIFIC HEAT OF LITHIUM HYDRIDE

Temperature, °K.	Specific heat:	
	Observed	Calculated
74·0	0·68	0·74
75·2	0·74	0·70
76·6	0·76	0·72
77·6	0·72	0·76
83·2	0·92	0·92
85·9	1·02	1·04
88·4	1·10	1·12
90·5	1·22	1·22
93·0	1·34	1·32
95·7	1·38	1·42
292·7	8·18	8·24

Heat of Formation and Heat of Hydrolysis.

The heat of formation of lithium hydride has been measured indirectly from the heats of hydrolysis of lithium and lithium hydride, and directly by measurement of the decomposition pressure: it has also been calculated from the absorption spectrum of the solid. The results of these measurements are in good agreement, as shown in Table V.

TABLE V. - HEAT OF HYDROLYSIS AND HEAT OF FORMATION OF LITHIUM HYDRIDE

Authors	Date	Method	ΔH_h kg.-cal./g.-mol.	ΔH_f kg.-cal./g.-mol.
Guntz[32]	1896	Calorimeter	-31·97	-21·61
Moers[5]	1920	Calorimeter	-31·62	-21·60 ± 0·25
Messer, Fasolino and Thalmayer[33]	1955	Calorimeter	-31·76 ± 0·10	-21·34 ± 0·15
Hurd and Moore[34]	1935	Vapour pressure	-	-22 ± 1
Kapustinskii, Shamovskii and Bayushkina[35]	1937	Absorption spectrum	-	-22·9(LiH) -23·6(LiD)

6·2

Calorimetric measurements of the heat of hydrolysis of the solid:-

$$\mathrm{LiH}_{(s)} + \mathrm{aq.} \rightarrow \mathrm{LiOH}_{\mathrm{aq.}} + \mathrm{H}_{2(g)};\ \Delta H_h,$$

and of the heat of hydrolysis of metallic lithium, have been made by three independent workers.[5,32,33] By comparing the two results, the heat of formation, ΔH_f may be obtained:-

$$\mathrm{Li}_{(s)} + \tfrac{1}{2}\mathrm{H}_{2(g)} \rightarrow \mathrm{LiH}_{(s)};\ \Delta H_f.$$

The most recent workers claimed greater accuracy on the grounds that they used lithium hydride of greater purity; their results[33] refer to infinite dilution at 25°C.

Other values for the heat of formation have been obtained by measurement, at various temperatures, of the vapour pressure, assumed to be entirely due to the hydrogen. The heat of the decomposition reaction ($-\Delta H_f$) was calculated in the usual way from a plot of log (pressure of H_2) against the reciprocal of the absolute temperature. Technically the measurements are very difficult, all authors[4,10,33,36] having failed to obtain reproducible results; the figures quoted in Table VI are either those the authors[10] regarded as fairly reliable or the result[33] of a single successful run.

TABLE VI. - DECOMPOSITION PRESSURE OF LITHIUM HYDRIDE

Authors	Date	Temp. °C.	Pressure, mm.
Hüttig and Krajewski[10]	1924	23	0·023
		150	0·05
		170	0·11
		190	0·34
Hurd and Moore[34]	1935	509	0·10
		597	1·85
		598·5	1·75
		649	7·30
		653	7·80
Guntz[32]	1896	680	26·8

Calculation of the heat of formation from the absorption spectrum of the solid is based on the assumption, already illustrated (see page 135) that the following equation may be used to evaluate ΔH_f:-

$$h\nu = -\Delta H_f + S + \tfrac{1}{2}D.$$

From the observations[35] (λ = 2517A. for LiH and λ = 2482A. for LiD) and the values 51·83 and 52·72 for half the dissociation energy of hydrogen and deuterium, respectively, the values for the heat of formation of the hydride and deuteride given in Table V were derived. From the same data the heat for the reaction:-

$$\mathrm{LiH} + \mathrm{D} \rightarrow \mathrm{LiD} + \mathrm{H},$$

was calculated to be 1·6 kg.-cal. per g.-mol.; the formation of the deuteride is exothermic, as is to be expected from its more rapid formation[4] than the hydride from the metal.

Irradiation[37] of solid lithium hydride with light of wave-length 2537A. liberates hydrogen in a 5% quantum yield; it is thought[37] that only interstitial hydrogen is thus liberated from the lattice.

Electrical and Magnetic Properties.

Electrolysis provided much of the original evidence for the conclusion that the solid is ionic. Electrolysis of the solid, *in vacuo*, using direct current, led to an increase in pressure[5] and the appearance of metallic lithium at the cathode. Later[38] it was proved that the gas was hydrogen and the yield is 99·5% of that calculated from Faraday's law (assuming an H^- ion), but the yield of metallic lithium is less than the calculated value because the metal is soluble in the hydride. The minimum potential required to release hydrogen is 0·1V.[39] More recently[40] it has been found that the optimum yield of hydrogen at the anode (>80% of the theoretical) can be obtained by passing a current through the solid at a temperature just below its melting point (680°C.) for 2·5 min.; if the temperature is raised or the duration of electrolysis increased the yield is reduced.

The solid is diamagnetic, having a molar magnetic susceptibility, measured[41] on a Gouy balance, of $-4{\cdot}60 \times 10^{-6}$ c.g.s. units (within 2%) at both 300°K. and 78°K. This experimental value is less than one half of the lowest of the various predicted values and the discrepancy is attributed[41] to temperature-independent paramagnetism. The most recent calculation,[42] based on the sum of the values for helium-type ions, is $-11{\cdot}6 \times 10^{-6}$ c.g.s. units.

An interesting suggestion was made[43] in 1935 that the ratio of the nuclear magnetic susceptibility to the diamagnetic susceptibility would be 0·12 at 2°K. and 0·06 at 4°K., so that at very low temperatures it might be possible to measure the nuclear susceptibility.

A number of physical properties have been calculated but not observed directly. For example, from the lattice energy the compressibility has been calculated[24] ($2{\cdot}36 \times 10^{-12}$). The repulsion exponent has also been calculated; the value,[24] 4·1, is in agreement with the value 3·9, derived[44] from spectroscopic data for the gas.[45] The dipole moment of the gaseous molecule has been calculated[46] as 4·05D., using an empirical rule[47] based on ion-pair molecules, compared with 3·5D. deduced[48] from quantum-mechanical considerations. For the gas, the entropy calculated[49] from spectroscopic data[50] is 38·77 entropy units at 298·1°K. For the solid the entropy derived[51] from specific-heat data[31] is 5·9 ± 0·5 entropy units at 298·1°K.

Absorption and Emission Spectra; Dissociation Energy of the Gas.

A great deal of spectroscopic work has been carried out on gaseous lithium hydride and lithium deuteride. The emission spectrum was obtained from a lithium arc[52] in an atmosphere of hydrogen at reduced pressure. Later[45] the emission spectrum (λ 3200–5000A.) was observed by the same technique, and the absorption spectra (λ 3000–4500A.) of mixtures of lithium and hydrogen vapours at various temperatures (600°–900°C.) and pressures (50–160cm.) were also observed; full details are given in the paper.[45] In appearance the spectra, due to $^1\Sigma \rightarrow {}^1\Sigma$ transitions, are like those of molecular hydrogen and consist of many lines forming bands which show P and R branches, the latter being degraded towards the red. It is possible to distinguish between the spectra of ^{7}LiH and ^{6}LiH and those of the corresponding deuterides. Full details of the frequencies and assignments for ^{7}LiD and ^{7}LiH have been given[53,54] (see also page 284).

There are four combinations of the isotopes, ^{6}Li, ^{7}Li, H and D, and shifts in the positions of the spectral lines have aroused considerable interest. Comparison[55,56] of ^{6}LiH and ^{7}LiH showed that the relative positions of the lines were approximately as calculated, but that the relative intensities did not correspond to the ratio of natural isotopic abundance, ^{6}Li:^{7}Li = 1:13; in fact, when the mixture of hydrogen and lithium vapours was first heated the relative intensities of the spectral lines corresponded to a ratio ^{6}LiH:^{7}LiH of 1:2, and on prolonged heating this changed to 1:8.[55] Thus, apparently ^{6}Li forms a hydride more rapidly than does ^{7}Li. Comparison[57] of ^{7}LiH and ^{7}LiD shows an anomaly in that the empirical ρ values of the bands, expected to be in the ratios of the reduced masses, are sometimes larger and sometimes smaller than expected. Correction for anharmonicity (interaction between rotation and vibration) makes the anomalies smaller but does not remove them altogether. It seems[57] probable that they arise from an unusual potential-energy curve for the excited state. Part of this curve was calculated from the observations.[57] Later,[58] another part of the curve was calculated by Klein's method[59] using Nakamura's postulate[45] that the dissociation of the excited state is into excited lithium atoms, Li(^{2}P), and normal hydrogen atoms. The two parts of the curve joined satisfactorily. Another version of this potential-energy curve, based upon a simple electrostatic calculation,[73] is in good agreement.

A summary of the results of spectroscopic investigation is given in Table VII. Further discussion may be found in a number of papers;[60] see also page 284.

TABLE VII. - RESULTS OF SPECTROSCOPIC MEASUREMENTS ON LITHIUM HYDRIDE

Authors	Date	Interatomic distances, A. ground state LiH	LiD	excited state LiH	LiD	Dissociation energy, electron volts per mol. LiH	LiD	Moment of inertia, 10^{40} g.sq.cm. LiH ground state	LiH, excited state
Watson[52]	1925	–	–	–	–	–	–	6	–
Nakamura[45]	1929	1·60	–	2·50	–	2·56	–	3·70	9·3
Crawford and Jorgensen[57]	1936	–	–	–	–	2·54 ±0·2	2·53	–	–
Crawford (see Knipp[66])	1936	–	–	–	–	2·63 ±0·05	–	–	–
Herzberg[61]	1950	1·5953	1·5949	2·5963	2·5859	2·5	2·5	–	–

Force constant for LiH, 6·5 × 10^5 dynes/cm.
Fundamental frequency, 1407 cm.$^{-1}$

For the gaseous molecule a number of theoretical calculations by different methods have led to the conclusion that ionic terms are important, and while, for a first approximation, the 1*s* electrons of lithium are assumed not to take part in bonding, more sophisticated treatments have shown that inclusion of these electrons makes a large difference to the calculated dissociation energy, *D*. Comparison of this with the observed value (2·5 e.V., see Table VII) is usually taken as a criterion for the correctness of the theory and the validity of the simplifying assumptions. At present, however, the best agreement is not given by the most rigorous treatments.

The earliest calculations[62,63] were based on the assumption that the molecule was entirely covalent and that the 1*s* electrons of lithium took no part in bonding. By the Heitler-London or electron-pair method[64] the following quantities were calculated:[63] interatomic separation, 1·44A.; *D*, 2·30 e.V.; and fundamental frequency, 1400 cm.$^{-1}$ Subsequent recalculation,[59] including a correction to one of the integrals, gave 1·53A., 1·30 e.V. and 1370 cm.$^{-1}$, respectively, results which indicated[65] that the assumption was not valid and that some ionic terms were required. Another early calculation (1934), based on the same assumptions and also on the assumption that the interatomic separation is 1·60A., gave D = 2·30 e.V. by a treatment exactly analogous to that for hydrogen by Hylleras.[65] Similarly in 1936 the application of a treatment[66] analogous to that of James and Coolidge[68] for hydrogen gave D = 1·89 e.V. At the opposite extreme, the assumption of complete ionization with each ion polarized in the field of the other gave,[46] by an empirical relationship,

D = 2·4 e.V. A simplification[67] of the molecular orbital treatment gave D = 1·855 e.V., and this corresponded to a model in which 66% of the electronic charge cloud of the binding electrons was situated on the hydrogen, 11% on the lithium and the remainder in overlap. The percentage ionic character calculated from the electronegativity difference (1·1) by an empirical formula[69] is 21·8. The most complete treatment[70] was carried out by the Hartree-Fock method. Four sets of calculations were made, viz. (a) for two electrons by the electron-pair method without ionic terms; (b), as for (a) but including ionic terms; (c) for two electrons by the molecular orbital method (linear combination of atomic orbitals); and (d) for four electrons by the molecular orbital method. The values of D were (a) 2·64 e.V., (b) 3·68 e.V., (c) 3·57 e.V. and (d) 2·0 e.V., at the observed interatomic distance. The equilibrium interatomic distances and fundamental frequencies were also calculated[71] by using the minimum-energy criterion, and as the variation from the experimental value was not more than 0·2A. it was concluded that the use of experimental interatomic distances would be justifiable in future calculations.[71] It is curious that the most rigorous treatment (*i.e.*, (d)) did not give the best value for the dissociation energy. The ratio of $2p$ to $2s$ in the hybridization was given as 0·41 by the most rigorous treatment and as less by the various approximations.[72] Quantum-mechanical calculation[74] indicated that LiH^+ would be unstable.

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Chemical Properties

Lithium hydride reacts vigorously with water, giving lithium hydroxide and hydrogen. In many reactions lumps of lithium hydride are surprisingly inert; for efficient reaction it must first be powdered, in an atmosphere of dry nitrogen. Its main reactions are of the replacement type, leading to the formation of hydrides of other elements and of double hydrides. It is a particularly useful reagent for replacing halogens by hydrogen.

Treatment[1] of lithium hydride with benzoyl chloride dissolved in a high-boiling hydrocarbon, at about 200°C. for 4 hr., leads to the formation of benzyl benzoate, which may be distilled off under reduced pressure, leaving lithium benzoate in the residue.

Alkyl and alkenyl silanes can be prepared[2] from the corresponding chlorides, e.g., $RSiCl_3$ and R_2SiCl_2, by treating them with lithium hydride. The reaction is carried out in *iso*amyl ether, in which lithium hydride is insoluble. Unsaturated hydrocarbon radicals are not normally hydrogenated, so that propenyl trichlorosilicon can be converted into the corresponding unsaturated silane; the yield is about 40%.

A similar reaction is observed[3] with alkyl aluminium halides and lithium hydride. For example, treatment of a warm ethereal solution of diethyl aluminium chloride, Et_2AlCl, with a suspension of lithium hydride in ether gives diethyl aluminium hydride and lithium chloride.

Ethoxides of aluminium and boron give either the hydrides of these elements or, in the presence of excess lithium hydride, double hydrides.[4] The reaction between an excess of lithium hydride and an ethereal solution of aluminium ethoxide proceeds by three stages:-

$$LiH + Al(OEt)_3 \rightarrow Li[HAl(OEt)_3](+ LiH) \rightarrow Li[H_2Al(OEt)_2] + LiOEt(+ 2LiH) \rightarrow LiAlH_4 + 2LiOEt$$

All the products containing aluminium are colourless crystalline compounds which are soluble in ether and react with water to liberate hydrogen.

Lithium aluminium hydride[5] can also be prepared by the action of lithium hydride (4g.) on aluminium chloride (2·7g.). The solids are mixed in an atmosphere of dry nitrogen and after the vessel has been evacuated, diethyl ether (15ml.) is distilled into the mixture at about −193°C. When the mixture is allowed to warm up, a vigorous reaction sets in, and this must be damped down by additions of liquid nitrogen. The reaction is completed in about five minutes. After the insoluble lithium chloride has been filtered off, the filtrate is evaporated to dryness under reduced pressure; the residue (2g.) is lithium aluminium hydride.

The disadvantage of this simple reaction is that it cannot be easily controlled. First, there is an induction period that may vary from a few minutes to several hours. Then, when the reaction does start, it proceeds with uncontrollable vigour and is complete within a few minutes. The reaction of gallium chloride with an excess of lithium hydride, on the other hand, proceeds smoothly to give lithium gallium hydride.

The best method of preparing lithium aluminium hydride involves the use of a small amount of this material as catalyst or 'promoter'. Solid lithium hydride (3mol.) is added to an ethereal solution of lithium aluminium hydride (0·08 mol. in 30 ml.). After the mixture has been well stirred, it is diluted with ether (200 ml.) and a solution of aluminium chloride (0·5 mol.) in ether (300 ml.) is added at such a rate as to keep the reaction mixture boiling gently. The insoluble lithium chloride and the excess of lithium hydride are filtered off. The product obtained after removing the ether from the filtrate has a purity of about 95%.

If the amount of lithium hydride used corresponds to that in the equation:-

$$3LiH + AlCl_3 \rightarrow 3LiCl + AlH_3,$$

or if aluminium chloride is added to a solution of lithium aluminium hydride, after the lithium chloride has been filtered off, evaporation of the ethereal solution gives a white solid in which the ratio of aluminium to hydrogen is 1:3, but the compound also contains ether which cannot be removed.

Lithium aluminium hydride decomposes at 125°C. giving aluminium, hydrogen and lithium hydride. It reacts vigorously with compounds containing hydroxyl groups, e.g., acids, alcohols and water, liberating hydrogen. With an excess of water the products are hydrogen, lithium hydroxide and aluminium hydroxide. It is a useful reagent for the reduction of ketones and esters to the corresponding alcohols. It reacts with halides and alkyl derivatives to give hydrides, e.g.:-

$$Me_2Zn + LiAlH_4 \rightarrow ZnH_2 + LiAlMe_2H_2$$
$$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + LiCl + AlCl_3$$
$$2Si_2Cl_6 + 3LiAlH_4 \rightarrow 2Si_2H_6 + 3LiCl + 3AlCl_3$$

With boron trichloride it gives diborane:-

$$3LiAlH_4 + 4BCl_3 \rightarrow 3LiCl + 3AlCl_3 + 2B_2H_6$$

Lithium aluminium hydride (0·277g.) dissolved in ether (5 ml.) is cooled in liquid nitrogen, and boron trichloride (1·279g.) is distilled into the vessel. A vigorous reaction takes place, presumably the formation of the complex between ether and boron trichloride, and when the mixture is allowed to warm up to room temperature, diborane is evolved in 99·4% yield. The action of diborane itself on lithium aluminium hydride leads to the formation of lithium borohydride and aluminium borohydride:-

$$LiAlH_4 + 2B_2H_6 \rightarrow LiBH_4 + Al(BH_4)_3$$

The simplest preparation is to pass gaseous diborane over lithium aluminium hydride at about 80°C. Aluminium borohydride is volatile and may be condensed in a cold trap while the lithium borohydride remains behind as the residue.

Diborane is also produced[6] by the action of lithium hydride on the ether complex of boron trifluoride:-

$$8BF_3,OEt_2 + 6LiH \rightarrow B_2H_6 + 6LiBF_4 + 8Et_2O$$

The boron trifluoride–ether complex is added to an ethereal suspension of finely powdered lithium hydride. The reaction starts at room temperature, and being exothermic, raises the temperature of the mixture to the boiling point of the ethereal solution. When the reaction has subsided, the mixture is refluxed for several hours, the volatile diborane being collected in a cold trap. Subsequently, the contents of the cold trap are purified by fractionation. This process is one of the most efficient for the preparation of diborane (80–95% yield) and has been patented.[7]

If this same reaction is carried out in the presence of lithium borohydride the course of the reaction is completely changed. Diborane is not evolved unless there is an excess of boron trifluoride present, and the products are lithium fluoride and lithium borohydride. It has been shown that the reaction proceeds in two stages. The first is the exothermic reaction to produce lithium borohydride:-

$$4LiH + BF_3 \rightarrow LiBH_4 + 3LiF;$$

then, in the presence of more boron trifluoride, endothermal decomposition sets in giving lithium fluoride and diborane:-

$$3LiBH_4 + BF_3 \rightarrow 2B_2H_6 + 3LiF.$$

The reaction with boron trichloride, on the other hand, gives lithium borohydride even in the absence of lithium borohydride to act as promoter. Similarly, boron trifluoride in the presence of ether and tetrahydrofuran will give lithium borohydride in the absence of a promoter. It has been suggested that the role of the promoter is to prevent contamination of the surface of the lithium hydride by insoluble complexes.

Direct reaction[8] between boron trifluoride and lithium hydride in the absence of ether does not lead to the production of diborane; the course of this reaction has not yet been elucidated.

If lithium hydride is treated with an ethereal solution of diborane, lithium borohydride is formed:-

$$2LiH + B_2H_6 \rightarrow 2LiBH_4$$

From the reaction of lithium hydride with methyl borate two intermediates, lithium boromethoxyhydride, $LiBH_2(OMe)_2$, and lithium boromethoxide, $LiB(OMe)_4$, have been isolated, in addition to the main end-product, lithium borohydride. It is believed that the primary reaction product is the unstable addition compound $LiBH(OMe)_3$.

It is stated[9] that, at 500°C. under reduced pressure, lithium hydride will reduce the chlorides of sodium, potassium, rubidium and caesium to give the free alkali metal and hydrogen. At the same temperature metallic lithium will react to form lithium chloride and the alkali metal, but the authors[9] considered that dissociation of the lithium hydride was not the primary reaction because the pressure of hydrogen (16–26mm.) was greater than the equilibrium pressure of hydrogen (0·07mm.) over lithium hydride at 500°C. No hydrogen chloride was evolved in the reaction. The same workers[9] carried out reactions between lithium hydride and the oxides of Group IVA and Group VA metals at 500°C.; they report difficulty in analyzing the products of the reactions but find that while thorium dioxide is not attacked, zirconium and silicon dioxides are reduced to the elements and that germanium and titanium dioxides and niobium pentoxide are reduced to lower oxides.

Two extensive review articles have been published on hydrides in general, one[10] written in 1926 and the other in 1953,[11] and in 1954 a review on lithium hydride only.[12]

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Uses

Lithium hydride has no large-scale uses. The following ideas, taken from the patent literature, show the directions of potential development.

6·4

Lithium hydride may be used[1] as a reducing agent for refractory oxides, with which it is mixed and heated, *in vacuo,* at 800–900° C. Elements that have been prepared in this way are chromium, beryllium, boron, zirconium, uranium and tantalum. The sulphur content of iron can be reduced to 0·009% by the addition of lithium hydride[2,3] at the slag-metal interface.

As a reducing agent it is a possible rocket fuel,[4] the oxidizing agents being the oxides, fluorides or oxyfluorides of nitrogen.

It has been used as a catalyst in a number of polymerizations, for example, in the polymerization of butadiene to synthetic rubber,[5] and in the production of analogues of 'Terylene'. Normal production of 'Terylene' is by ester interchange between methyl terephthalate and ethylene glycol; these are heated under reduced pressure and the methanol is pumped off. Various catalysts, including lithium hydride[6,7] have been suggested for reactions between alkyl terephthalates and polyethylene glycols.

Electrolysis[8] of an anhydrous diethyl ether solution of 2–3M. aluminium chloride and 0·5–1·0M. lithium hydride at 5 amp./sq. in. gives a ductile deposit of aluminium.

Perhaps the most important use is in the production of lithium aluminium hydride,[9] which is finding increasing application in the field of organic chemistry.

Lithium hydride has limited use as a convenient method of transporting hydrogen[10] because it liberates one-quarter of its weight of this gas on the addition of water.

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SECTION VII

LITHIUM OXIDE

By R.E. OLIVER

PREPARATION AND PRODUCTION

Lithium oxide may be prepared by direct combination; despite the extreme readiness with which the elements combine, it is difficult to carry out the reaction under controlled conditions, owing to the protective film of oxide formed on the surface of the metal. Direct combination is better undertaken in a liquid-ammonia system.[1] Lithium metal (1·5 g.) is dissolved in liquid ammonia (30 ml.). A blue solution results. Oxygen is passed in until the solution is colourless, and the ammonia is then removed by evaporation. The product contains approximately 23% of lithium peroxide and 77% of lithium oxide. Heating to 300°C. decomposes the peroxide present, leaving a pure lithium oxide sample.

Lithium hydroxide may be decomposed by heating in vacuum[2] according to the equation:

$$2\,LiOH \rightarrow Li_2O + H_2O\uparrow$$

The reaction is carried out in platinum, and at 1000°C. is complete after several hours.

Lithium carbonate may be decomposed in a similar manner:[3,4]

$$Li_2CO_3 \rightarrow Li_2O + CO_2\uparrow$$

Again the reaction is carried out in platinum, with the decomposition temperature in the range 700–1000°C.

Two further laboratory preparations are described below.

(i) To a saturated solution of lithium hydroxide in ethyl alcohol at 95°C. is added the theoretical quantity of perhydrol.[1] Lithium peroxide is precipitated, which after washing with alcohol is decomposed to lithium oxide by heating to 300°C. Very pure samples of the oxide may be made in this way.

(ii) Lithium metal (2 g.) is dissolved in ethyl alcohol (250 ml.) under an atmosphere of helium.[5] Lithium ethoxide is precipitated; this is filtered and washed with alcohol. It is then slurried with a further 250 ml. of alcohol, and 25 ml. of 30% hydrogen peroxide are added. After stirring for several hours, LiO_2H,H_2O separates in approximately 56% yield; this compound is dehydrated at 20 mm. pressure over phosphorus pentoxide to give lithium peroxide, which is then decomposed to the oxide by heat.

PHYSICAL PROPERTIES

Structure.

The crystal structure of lithium oxide is cubic and of the anti-fluorite type, with oxygen replacing calcium and lithium replacing fluorine in the fluorite lattice.[3,6,7] The lattice parameter is 4·619 A.[7] Lithium atoms lie at the centres of perfect oxygen tetrahedra.[3] The interatomic distances[3] are:

Li–O	2·00 A.
Li–Li	2·32 A.
O–O	3·27 A.

The molecular volume of lithium oxide is 8·3 c.c.[8]

Density.

The density of lithium oxide is 2·02 g./c.c.[6]

Melting Point.

There are two recently published values, which however are not in agreement:

1427 ± 15°C.[9]
1570°C.[14]

Volatility and Stability.

Early work on the volatility of lithium oxide[11] is very conflicting and in many cases is vitiated by the presence of water. The apparent volatility in the presence of traces of water is much higher, owing to the volatilization of very stable lithium hydroxide molecules.

Lithium oxide samples have been heated to 1000°C. in magnesia boats, both under vacuum and in the presence of oxygen.[12] Losses in weight were proportional to the initial quantity of lithium oxide, indicating that they were a function only of the impurities present. The volatilization of lithium oxide at this temperature is insignificant. The vapour pressures of lithium oxide and lithium in equilibrium at 1000° K. are:

Li_2O 1×10^{-4} atm.
Li 1×10^{-12} atm.[13]

This is a point of difference between lithium and the other alkalis,[13] for which the magnitude of these values is reversed. There is no indication of appreciable volatility even at 1570°C.[10]

It has been shown by calculation that the vaporization of lithium oxide as its gaseous elements alone is unlikely, since the experimental vapour pressures are higher than the calculated values.[9] It is thought more likely that the vapour also contains molecules of lithium oxide, and under oxidizing conditions molecules of LiO.

Conductivity and Electrode Potential.

The conductivity of molten lithium oxide has been determined.[14] Fused magnesia crucibles were prepared by drilling large synthetic crystals. The crucible was placed in a carbon crucible and heated by induction under an atmosphere of argon. The electrodes were made from 40% rhodium/platinum alloy which was found to be almost completely resistant to the melt. Up to 20% of the lithium oxide present attacked the crucible, but the conductivity was found to be independent of the magnesium oxide concentration. The equivalent conductivity at 1570 °C. was 108 $ohm^{-1}cm.^{-2}$ ± 20%.

The electrolyte behaviour of some fused silicate systems including Li_2SiO_3 has been studied.[15-18] Within the experimental error the conduction has been shown to be wholly ionic. The system was studied under vacuum in a molybdenum cell at temperatures up to 1800°C.; a carbon anode was used. Measurement of the oxygen liberated showed that Faraday's Laws were obeyed. Apparent deviations were due to secondary reactions at the electrodes. The conductivity increases with increase in concentration of lithium oxide.

Lithium oxide is completely ionized in fused cryolite and fused lithium metaborate.[19]

The electrode potential of lithium oxide in molten lead silicate has been studied.[20] In a cell of the type

$$- Pt : O_2 \mid PbSiO_3 + Li_2O \mid PbSiO_3 \mid O_2 : Pt +$$

the negative potential increased with increasing concentration of lithium oxide, and also in the order:

$$K_2O > Na_2O > Li_2O,$$

indicating that the electrodes respond to the oxygen-ion activity as a function of the concentration and basicity of the oxides dissolved in the melt. In the lithium oxide–lead silicate system an almost linear relationship was found between concentration of lithium oxide and electrode potential.

Concentration	Electrode Potential
0·4 mole Li_2O / 1 mole $PbSiO_3$	–400 mV.
0·1 mole Li_2O / 1 mole $PbSiO_3$	–190 mV.

Heat Content.

Values are listed in Table I.

TABLE I.- MOLAL HEAT CONTENT OF LITHIUM OXIDE ABOVE 298·16°K.[21]

Temp. °K.	$H_T - H_{298 \cdot 16}$ (g.-cal.)
427·7	1836
515·0	3303
625·2	5208
690·6	6403
823·8	8925
954·4	11529
1045·1	13376

Systems Containing Lithium Oxide.

These are considered under the section dealing with the application of lithium oxide in the glass industry.

CHEMICAL PROPERTIES

Lithium oxide is a powerful base, analogous in almost all respects to sodium and potassium oxides. It reacts readily with water to give the hydroxide and with numerous acidic substances to give the corresponding lithium salts. Owing to the lengthy nature of its preparation, it is seldom used as such, the hydroxide and carbonate usually providing a convenient alternative for wet and dry reactions.

Several high-temperature reactions of lithium oxide have been studied in recent years.

A phase diagram constructed from thermal analysis curves[22] has shown the existence of further lithium borates in addition to the well-known monoborate $LiBO_2$ and diborate $Li_4B_2O_7$. New phases (decomposition temperatures in parentheses) corresponding to $3Li_2O,B_2O_3$ (695°C.), $3Li_2O,2B_2O_3$ (685°C.) and $Li_2O,3B_2O_3$ (835°C.) have been identified.

The reaction between silica and lithium oxide[23] gives first the metasilicate, Li_2SiO_3. The melting point of the metasilicate is 1201°C., but it may be formed by sintering at a substantially lower temperature (800–900°C.). At higher temperatures the metasilicate will react with further lithium oxide to give an orthosilicate, Li_4SiO_4 (m.p. 1250°C.). As the temperature is further raised, the addition of lithium oxide gives Li_6SiO_5 and then Li_8SiO_6. The rate of reaction of silica with the alkali-metal oxides[24,25] is in the order

$$K_2O > Na_2O > Li_2O$$

and practical relationships have been derived based on the silica particle-size. A sharp increase in the rate occurs at 870°C., caused by the rapid disruption of SiO_4 tetrahedra in the inversion of quartz to tridymite. Fused Li_2SiO_3 has been electrolyzed.[26] Lithium is produced at the cathode, but reacts with the melt to liberate silicon. This secondary reaction results in the formation of a series of lithium–silicon alloys and Li_6Si_2.

In the reaction between lithium oxide and alumina[23] two products are formed according to the equations:

$$Li_2O + Al_2O_3 \rightarrow 2LiAlO_2;$$
$$3Li_2O + Al_2O_3 \rightarrow 2Li_3AlO_3.$$

Finely divided zirconia reacts slowly with lithium oxide to give $LiZrO_3$. Conversion is complete after 3 hr. at 1350°C.[27]

In a similar manner lithium oxide will react with germanium dioxide to give Li_2GeO_3 (m.p. 1237 ± 3°C.) which with further lithium oxide gives Li_4GeO_4 (m.p. 1295 ± 3°C.).[28]

Lithium oxide reacts with vanadium pentoxide to form the three normal vanadates[29] $LiVO_3$ (m.p. 618°C.), $Li_4V_2O_7$ and Li_3VO_4. When lithium metavanadate reacts with further quantities of V_2O_5 compounds known as vanadyl vanadates[29,30] are formed. Oxygen is evolved and this is thought to be due to the reduction of V_2O_5 to V_2O_4, giving compounds of the type:

$$5Li_2O,V_2O_4,11\ V_2O_5;$$
$$9Li_2O,V_2O_4,23\ V_2O_5;$$
$$3Li_2O,V_2O_4,11\ V_2O_5.$$

These compounds have certain applications as semi-conductors.

APPLICATIONS

Lithium oxide is very widely used as a constituent of glasses. Several attempts have been made to classify the components of glasses and to forecast the effect of change of concentration, substitution, and addition of constituents. Such classifications include a scale of decreasing acidity,[31] the effect of various oxides on surface tension,[32] and a measure of the strength of bonding in the system, given by the expression z/a^2, where z is the valence of a given cation and a its distance from adjacent oxygen ions.[33]

A summary of the behaviour of lithium oxide with respect to the change in properties of some of the systems containing it is given below.

Silicate and Borosilicate Systems.

In the system Li_2O–SiO_2 a glass is formed on cooling melts containing up to 20% Li_2O.[34,35] If larger quantities of Li_2O are present[36] devitrification sets in rapidly at 500–600°C. and is complete at room temperature. Glasses containing up to 50·09% Li_2O have been studied and the volatilization of Li_2O from the melt observed. A system containing 38·22% Li_2O had a vapour pressure of 0·50 mm. at 1300°C. and lost 41 mg. Li_2O per sq. cm. of melt surface in 20 hr. An equilibrium diagram of the system shows the existence of three compounds, $2Li_2O,SiO_2$, Li_2O,SiO_2 and $Li_2O,2SiO_2$.[37] Melts in the system Li_2O–B_2O_3–SiO_2 devitrify on cooling. To obtain a stable glass it is necessary to add alumina.[34] Such glasses have application as solder glasses.[38]

Al_2O_3–B_2O_3–SiO_2 glasses containing approximately 14% Li_2O have been made with electrical resistivities in the range $10^9 - 10^{10}$ ohms per cm. cube. These values compare with 10^{13} for soda-lime glasses at room temperature. Dielectric constants have also been measured.[34]

The effect of substituting Li_2O for Na_2O and K_2O in the systems Na_2O–SiO_2 and K_2O–SiO_2 has been studied.[39] A maximum density was found when the ratio was 1:1. Improved chemical resistance was observed.

Several compounds in the Li_2O–K_2O–SiO_2 system were identified:

$$Li_2O,K_2O,4SiO_2,\ \text{m.p. } 870°C.;$$
$$Li_2O,2K_2O,6SiO_2,\ \text{m.p. } 815°C.;$$
$$2Li_2O,5K_2O,7SiO_2,\ \text{m.p. } 900°C.;$$

$Li_2O,5K_2O,7SiO_2$, m.p. 880°C.;
$Li_2O,5K_2O,4SiO_2$, m.p. 830°C.

The partial replacement of Na_2O by Li_2O in the system Na_2O–CaO–SiO_2 has many advantages.[40] The glasses formed smelt and fire well and have a lower softening point. Additions of small quantities of lithium oxide enable glasses of low expansion coefficient in this system to be smelted. The lithium may be added as lepidolite, which therefore includes the addition of alumina, resulting in glasses of improved chemical resistance.

The addition of small quantities of lithium oxide to the crystallization of cristobalite at 1400°C. resulted in the formation of tridymite.[41]

The effect of replacing sodium or potassium oxide by lithium oxide in iron-containing glasses[42] is to give a higher proportion of ferrous iron in the structure, with a resulting diminution of ferrosoferric oxide (Fe_3O_4), ferric oxide and colourless iron (structure building units analogous to SiO_4 tetrahedra).[43] In a K_2O–Na_2O–PbO–SiO_2 glass containing iron, ferric oxide is very stable. The effect of introducing lithium oxide is to form some ferrosoferric oxide, indicating that the greater mobility and field strength of lithium over sodium and potassium has reduced some of the iron to the ferrous state.

In the glass system Na_2O–(MgO–CaO)–SiO_2[44] the substitution of Li_2O for Na_2O gradually decreases the liquidus temperature in a system containing 14% Li_2O, 12% CaO and 74% SiO_2. In a 18% Li_2O, 10% CaO and 72% SiO_2 system it had little effect. The addition of lithium oxide reduced the resistance to attack by water and dilute sulphuric acid. Sodium and potassium oxides gave the highest resistance to attack, while any pair of alkalis was an improvement upon the alkalis individually. Addition of lithium oxide greatly decreased the deformation temperature in both series.

The Winkelmann and Schott factors for effect upon thermal expansion[45,46] are Na_2O 10, and K_2O 8·5. Most recent work indicates that lithium oxide is as effective as sodium oxide in promoting high expansibility.

In the system Na_2O–(MgO–CaO)–SiO_2 addition of lithium oxide[44] caused large increases in the coefficient of expansion.

In the system Li_2O–CaO–SiO_2, weight for weight substitution of sodium oxide for lithium oxide resulted in a decrease of coefficient of expansion,[47] while mole for mole substitution resulted in an increase. In each case the softening point was raised.

In the systems Na_2O–(MgO–CaO)–SiO_2[44] and Na_2O–CaO–SiO_2[43] the addition of lithium oxide in all cases reduced the viscosity. More general investigation[48,49] has shown that the viscosity of silicate melts depends upon the following factors:

(i) the number of cations introduced into the lattice;
(ii) the ionic radius of the cations;
(iii) the valency of the cations;
(iv) the number of discontinuities in the network of silicon–oxygen tetrahedra;
(v) the O/Si ratio (the greater the ratio the lower the viscosity).

The effect of the ionic radius of univalent cations upon the viscosity shows a reversion with increasing ion concentration; thus potassium oxide at low concentration increases viscosity but at concentrations above R_2O:SiO_2= 1:1 it lowers the viscosity to a greater extent than lithium oxide, which is ineffective in lowering viscosity both from ionic radius and from concentration considerations. Bivalent cations lower viscosity more than univalent cations.

At 1300°C., Li_2O 26 mol.-%, SiO_2 74 mol.-% has a surface tension of 332 dynes/cm.,[50] and Li_2O 36 mol.-% SiO_2 64 mol.-%, 334 dynes/cm. This increase in surface tension is contrary to the behaviour of potassium and sodium oxides and has been further demonstrated[51] in the systems Na_2O-SiO_2, $Na_2O-CaO-SiO_2$ and borosilicate glasses.

The partial molal surface tension of lithium oxide is 450 dynes/cm.[32]

The power factor (tan δ) has been measured on borosilicate glasses containing varying quantities of both lithium and sodium.[52] Increase in the Li/Na ratio caused increases in the power factor. Addition of lithium oxide to the $Na_2O-Al_2O_3-B_2O_3-SiO_2$ system gives glasses having very low values of loss angle measured at a frequency of 1 megacycle/sec.[34] A typical glass having a tan δ value of 0·0016 is: SiO_2 49·6, B_2O_3 20·8, Al_2O_3 9·0, Na_2O 13·9, Li_2O 6·7%.

Normal values for soda-lime-silica glasses are around 0·008.

In a study of the system $Li_2O-Al_2O_3-SiO_2$[53] the join Li_2O,SiO_2-β-eucryptite, ($Li_2O,Al_2O_3,2SiO_2$) was shown to be a simple binary with a eutectic at 1070°C. containing 57% β-eucryptite. The refractive index of the glasses decreased from 1·560 to 1·546 with increasing β-eucryptite concentration. The phase equilibrium along the join SiO_2-β-eucryptite has been investigated with equipment controlling both temperature and pressure.[54] Eucryptite, spodumene and petalite could all be synthesized.

Some thermal expansion coefficients (in cm./cm./°C., at 30-500°C.) of lithium aluminium silicates are cited:[46]

$Li_2O,Al_2O_3,2SiO_2$	$76{\cdot}0 \times 10^{-7}$
$Li_2O,Al_2O_3,4SiO_2$	$66{\cdot}6 \times 10^{-7}$
$Li_2O,Al_2O_3,6SiO_2$	$52{\cdot}5 \times 10^{-7}$
$Li_2O,Al_2O_3,8SiO_2$	$43{\cdot}6 \times 10^{-7}$
$Li_2O,Al_2O_3,10SiO_2$	$39{\cdot}3 \times 10^{-7}$

$Li_2O,Al_2O_3,2SiO_2$ devitrified on cooling to 500°C.

Compositions near the ratio $Li_2O-Al_2O_3-2SiO_2$ always yield β-eucryptite when fired in air above 970°C. β-Eucryptite shows the unusual property of continuous thermal contraction from 1000°C. to room temperature.[56]

Phase equilibria in the system $Li_2O-MgO-SiO_2$[55] showed primary fields of crystallization of tridymite, cristobalite, $Li_2Si_2O_5$, Li_2SiO_3, $MgSiO_3$, Mg_2SiO_4 and a new compound, Li_2O,MgO,SiO_2. The primary field for this compound is mainly below the Li_2SiO_3-forsterite join.

The cordierite-spodumene join has been studied in the system $Li_2O-Al_2O_3-MgO-SiO_2$.[57] At high temperature the phase diagram shows a small region of solid solution on the cordierite side, appreciable solid solution on the spodumene side, and regions of three or four phases, including α-cordierite, mullite, spinel, corundum and β-spodumene. The liquidus has a minimum between 40 and 50% cordierite at 1347°C., rising to the melting points of spodumene at 1421°C. and cordierite at 1530°C.

The ternary system $Li_2O-BaO-SiO_2$ has been used[58] to confirm the theory of Dietzel,[33] who had predicted that no ternary compounds would be formed. Only the binary silicates of the partial systems $Li_2SiO_3-SiO_2$, $Li_2SiO_3-BaSiO_3$ and $BaSiO_3-SiO_2$ were identified. The invariant points are all eutectics with the characteristics shown below.

System	Melting Point (°C.)	Composition (%)
Li_2O,SiO_2-BaO,SiO_2	970	SiO_2 50, BaO 26, Li_2O 24
$Li_2O,2SiO_2-BaO,2SiO_2$	960	SiO_2 66·5, BaO 12, Li_2O 21·5
$Li_2O,SiO_2-BaO,SiO_2-2BaO,3SiO_2$	940	SiO_2 53, BaO 24·5, Li_2O 22·5
$Li_2O,SiO_2-Li_2O,2SiO_2-BaO,2SiO_2$	910	SiO_2 65·5, BaO 12·5, Li_2O 22
$Li_2O,SiO_2-BaO,2SiO_2$-tridymite	920	SiO_2 67, BaO 12, Li_2O 21

Refs. p. 156

Borate Systems.

The system Li_2O–B_2O_3 has been extensively studied. Melts containing up to 10% Li_2O give glasses on cooling.[34] Determinations of density in the range 600–1000°C. in the liquid system have been carried out by the counter-balanced-sphere method.[59] At room temperature there is a linear increase in density with the addition of lithium oxide up to approximately 30 mol.-%. At 800° and 1000°C. the increase is again linear but rising more steeply up to 15 mol.-% and showing a maximum at 30 mol.-%. Over the temperature range 25–1000°C. expansivity was high for low lithium oxide content, showed a minimum at 10% and then increased. In the low lithium oxide region expansivity in the liquid range decreased with increasing temperature, while in the high lithium oxide range, the reverse was true.

The refractive index also increases with lithium oxide content, while the molecular refraction and molecular volume decrease.[60] Lithium glasses exhibit straight-line functions for their properties and optical constants, and it is thought likely therefore that lithium ions enter the borate structure, filling gaps which are present in the lattice, without distortion.

Viscosity and electrical resistivity have also been determined.[61] Isotherms of log viscosity (η) in the range 700–800°C. showed a minimum in the low-alkali region and a maximum as the lithium oxide concentration increased. The electrical resistivity decreased rapidly with increasing lithium oxide content, with a corresponding rapid increase in the equivalent conductivity.

Surface tensions in this system have been measured by means of the pull exerted on a thin-walled platinum cylinder with its lower edge in contact with the liquid.[62] Lithium oxide raised the surface tension of the melt. Comparative figures (at 1000°C.) are:

B_2O_3	83·5 dynes/cm.
B_2O_3,10·6% Li_2O	141·7 dynes/cm.
B_2O_3,20·1% Li_2O	201·6 dynes/cm.

In the high-alkali range the effectiveness of the common alkalis in raising surface tension was Li > Na > K, whereas in the low-alkali range the order was reversed.

The dielectric loss of Li_2O–B_2O_3 glasses[63] is higher than that of similar soda or potash glasses. The value shows a minimum at approximately 9 mol.-% Li_2O.

In the system Li_2O–Al_2O_3–B_2O_3[64] the region of easily fusible glasses has been studied, and the following generalizations put forward:

(i) Lithium ions do not cause a contraction of glass in the whole-glass region, but only in the destruction region.

(ii) Devitrification takes place readily in the destruction region, where glass is being contracted, but only with great difficulty in the accumulation region.

(iii) The components of the devitrified glass are $LiBO_2$, $Li_2B_4O_7$ and $9Al_2O_3,2B_2O_3$.

(iv) Addition of alumina reduces thermal expansion only up to the transformation region; beyond this region expansion is increased. A substantial decrease in the coefficient of expansion is caused when the composition is $Li_2O,4B_2O_3$.

(v) The point of transformation and softening point are maximal at a ratio $Li_2O,2B_2O_3$ containing up to 10 mol.-% Al_2O_3.

(vi) The thermal coefficient of electrical conductivity is higher in the accumulation region than in the destruction region.

The system Li_2O–BeO–B_2O_3 forms the basis of Lindemann glasses. These glasses find application in the windows of X-ray tubes owing to their high X-ray transmittancy.[65] The absence of silica in these glasses makes them readily attacked by moisture in the atmosphere.

The densities of glasses in the system range from 2·014 to 2·271 and the refractive indices from 1·498 to 1·561.[66,67] Lithium oxide increased the density of the glass, and if the proportion of boric oxide was high, increased its chemical stability.[68] The softening point of these glasses is approximately 500°C. Typical glasses resistant to crystallization and transparent to *X*-rays are:

	(a)	(b)
BeO	14·1%	11·6%
Li_2O	17·5%	17·7%
B_2O_3	68·4%	70·7%

Crystallization of glasses of this type is thought to be due to the formation of $3BeO,B_2O_3$, $LiBO_2$ and $Li_2B_4O_7$.[69,66] Substitution of Na_2O or K_2O for Li_2O causes only small changes in density and refractive index[70] but reduces corrosion resistance.

Similar properties are shown by the system Li_2O–MgO–B_2O_3.[65,70] The densities are in the range 1·91–2·38 and the refractive indices 1·49–1·56, both increasing with magnesia content.[71]

Phosphate Systems.

The system Li_2O–P_2O_5 has been investigated.[72] Changes in density, refractive index, molar volume and molar refraction were found to be non-linear with additions of lithium oxide. The effect of adding this oxide to phosphate glasses was studied by plotting the Abbé number against increasing molar concentration.[73] A smooth curve resulted; this was interpreted as normal behaviour in that lithium ions were introduced into the lattice without breaking down the tetrahedral structure around phosphorus atoms.

Other Glasses.

Additions of lithium oxide to various barium or lead tellurite glasses have been reported.[74] These glasses have a very high refractive index and low softening point, together with very good infra-red transmission to beyond 5·5 μ. A typical glass has the composition TeO_2 81–92, PbO 5–18, Li_2O 1–3%. The addition of lithium oxide increases the expansion coefficient and reduces the deformation temperature, in this case to 270°C. The refractive index is 2·14, and glasses of this type have higher resistivity than the more common soda-lime-silica glasses.

Similar glasses obtained by substituting germanium for tellurium[75] again have their properties enhanced by additions of lithium oxide. An infra-red transmission of 20–35% at 6 μ, together with high opacity to *X*-rays and good resistance to chemical attack, is claimed.

Glazes and Enamels.

In addition to its wide application in the manufacture of glasses, lithium oxide frequently imparts desirable properties to enamels and glazes.

Substituting Li_2O for Na_2O on a molecular basis in vitreous enamels improved fusibility, gloss, opacity and gave increased resistance to gouge, abrasion and acid attack.[76] Substituting on a weight basis, however, increased fusibility and increased gloss slightly, but decreased resistance to gouge, abrasion and acid attack. A decrease in opacity was observed. The substitution of spodumene for felspar in these enamels gives the advantages of lithium oxide addition. High-grade lepidolite may also be used as a source of lithium oxide.[77]

Small additions of lithium oxide to ground-coat enamels for steel sheet in general raise the surface tension of the melt.[51] In enamels of this type many attempts have been made to reduce or dispense with the boric oxide content. Where this has been achieved lithium oxide may be employed to reduce surface tension.[78]

The effect of additions of lithium oxide to titania cover-coat enamels has also been investigated.[79,80] Replacement of 1 part of potassium oxide by 1 part of lithium oxide resulted in an increase in reflectance and decrease in fluidity. If 3 parts of lithium oxide replaced 1 part of potassium oxide, the reverse effect occurred. Additions of lithium oxide increased resistance to acids and to abrasion.

To obtain an enamel of high electric strength the alkali content, especially the lithium and sodium oxide contents, must be maintained as low as possible.[81]

Addition of lithium oxide to whiteware glazes in general sharply reduces surface tension, enabling the glaze to mature at a lower temperature. Improved gloss and general quality are reported.[51]

Lithium oxide is used in the production of monoclinic zirconium dioxide for opacifiers in paints and glazes.[82] The conversion of amorphous or tetragonal zirconia to monoclinic zirconia occurs above 600°C. Trace impurities cause discoloration and slagging. These difficulties are readily overcome by the addition of up to 5% Li_2O, which acts as a catalyst in the conversion.

Lithium oxide combined with strontium oxide has been found to be an excellent substitute for lead oxide in dinnerware glazes.

Phosphors.

An Al_2O_3-Li_2O-Fe_2O_3-SiO_2 phosphor is described.[83] It is efficiently excited by a 2537 A. radiation, emitting a band spectrum with its energy peak at 6800 A. A typical composition is Al_2O_3 84·1, Li_2O 7·5, SiO_2 8·2, Fe_2O_3 0·2%. After firing for 2 hr. at 1250°C., considerable quantities of lithium oxide can be leached out with acid without reducing the fluorescence, but the total absence of lithium causes complete loss of fluorescence.

Thermally stable phosphors may be protected by coating with a readily fusible glass.[84] A mixture of phosphor and finely divided low-melting glass is spread over a soda-lime glass and heated for 30 min. at 600–700°C. in an inert atmosphere. A suitable glass is of the composition: SiO_2 20, Al_2O_3 3, MgO 2, Li_2O 2, Na_2O 5, K_2O 2, B_2O_3 66%. In this way composite phosphor layers can be built up.

Semiconductors.

The mechanism of oxidation and corrosion processes in metals and alloys has been widely studied. Lithium oxide vapour has been found to inhibit the oxidation of nickel and cobalt and accelerate that of titanium.[85-87] This phenomenon is thought to be due to the change in defect concentration in the oxide layer caused by the formation of solid solutions with lithium oxide.

Nickel may be protected in this way by heating in lithium oxide vapour at 1000°C.[88] The rate of oxidation at higher temperatures is frequently determined entirely by the diffusion of ions and electrons through the products of oxidation. Lithium oxide becomes incorporated in the lattice and reduces the number of vacant Ni^{2+} sites and thereby the oxidation rate. The rate of reduction of nickel oxide to nickel by hydrogen is decreased by the presence of lithium oxide, owing to an increase in the activation energy.[89]

The electrical properties of compounds of the Li_2O-NiO type have been studied, with a result that they have been developed as semiconductors. It has been found that the specific resistivity of various metal oxides which are non-conductors in the pure state can be lowered considerably by incorporating foreign metal oxides into them. It is necessary for the ionic radius of the foreign metal to be similar to that of the parent, but that its ionic charge should differ by at least one unit from the parent metal ion.[87]

The change in lattice parameter caused by the introduction of the second oxide may be followed either by electron diffraction or by *X*-ray back-reflection.[90,91] Lattice expansion gives rise to *n*-type conductivity and lattice contraction to *p*-type. The addition of lithium oxide to nickel oxide results in lattice contraction; this is thought to be due to the formation of Ni^{3+} ions having an ionic radius of 0·35 A., against the 0·78 A. of both Ni^{2+} and Li^+.[92] An equation to account for the formation of Ni^{3+} has been put forward by Verwey:[90]

$$n\mathrm{Li_2O} + 2(1-n)\mathrm{Ni^{2+}O} + \tfrac{1}{2}n\mathrm{O_2} \rightarrow 2\mathrm{Li}_n\mathrm{Ni}^{2+}_{1-2n}\mathrm{Ni^{3+}}_n\mathrm{O}$$

In the formation of $NiO-Li_2O$ the colour changes from grey-green to black with increasing lithium content.[93] The addition of 10% Li_2O causes a drop in resistivity from 10^8 to 1 ohm/cm.[94] Intermediate resistivity values are:

0·0025%Li	9530 ohm/cm.
0·9%Li	1·27 ohm/cm.[95]

The conductivity of this system is independent of oxygen pressure, and is attributed to the considerable increase in the concentration of electron-deficient sites (Ni^{3+}). In the system $ZnO-Li_2O$ the increase in the concentration of quasi-free electrons is insufficient to produce oxygen-pressure independence.[96] The system $CoO-Li_2O$ behaves very similarly to the $NiO-Li_2O$ system.[87]

The conductivity of calcium oxide has been determined: Above an oxygen pressure of 10^{-2} mm. calcium oxide is a defect conductor, while below it, it is an electron-excess conductor. Additions of lithium oxide give defect conduction even in high vacuum.[97]

Semiconductors of the Li_2O-NiO and Li_2O-ZnO types may be used as catalysts in certain oxidation reactions. Addition of lithium oxide to the *n*-type conductor zinc oxide increases the activation energy for carbon monoxide oxidation, but decreases it for the decomposition of nitrous oxide. Addition of lithium oxide to the *p*-type nickel oxide has the opposite effects.[98]

Lithium vanadyl vanadates[30] are semiconductors (see p.149) having electrical conductivities in the region of 0·1 $ohm^{-1}cm.^{-1}$.

RADIATION CHEMISTRY

Some compounds in the system $Li_2O-Al_2O_3-SiO_2$ are satisfactory sources of positive ions.[99] The sample is heated to 900–1000°C. on a platinum strip in vacuum. The emission of current is thought to be due to a change in the ratio of ^6Li to ^7Li. The compound $3Li_2O,Al_2O_3,3SiO_2$ gave a current of 4×10^{-4} amp./cm.^{2} for 40 hr. Spodumene ($Li_2O,Al_2O_3,4SiO_2$) may also be used.

Lithium oxide has been bombarded with α-particles and deuterons.[100] The target was prepared by depositing lithium oxide on gold leaf. The following reactions were observed:

10-Me.V. deuteron bombardment:

^{16}O (d, p) ^{17}O	
^{16}O (d, d) ^{16}O	(higher energy level)
^{16}O (d, α) ^{14}N	
^{7}Li (d, p) ^{8}Li	
^{7}Li (d, d) ^{7}Li	(higher energy level)
^{7}Li (d, α) ^{5}He	

20-Me.V. α-particle bombardment:

^{16}O (α, α) ^{16}O	(higher energy level)
^{7}Li (α, p) ^{10}Be	
^{7}Li (α, d) ^{9}Be	
^{7}Li (α, t) ^{8}Be	
^{7}Li (α, α) ^{7}Li	(higher energy level)
^{6}Li (α, α) ^{6}Li	(higher energy level)

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SECTION VIII

LITHIUM HYDROXIDE

By R.E. OLIVER

Preparation and Production

Lithium hydroxide is formed by the action of water on lithium metal or lithium oxide according to the equations:

$$2Li + 2H_2O \rightarrow 2LiOH + H_2\uparrow$$

$$Li_2O + H_2O \rightarrow 2LiOH$$

Preparation by these methods is in general of academic interest only. A simple laboratory mode of preparation is the double decomposition of lithium sulphate and barium hydroxide solutions.[1]

$$Li_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 + 2LiOH$$

If exactly equivalent quantities are used, a pure dilute solution of lithium hydroxide remains after filtration.

The preparation of lithium hydroxide on a small scale by electrolysis has been described.[2] A 30–35% solution of lithium chloride is electrolysed at approximately 10V. between a platinum anode and a mercury cathode. The cathode is circulated to maintain a concentration of 0•004% Li in the amalgam which is decomposed by water to give a dilute lithium hydroxide solution. Vigorous recycling of the electrolyte at a temperature of 45°C. gives a current efficiency of 95%. The product, though free from chloride, sulphate and iron, contains up to 2% of lithium carbonate.

Lithium hydroxide is a common starting material in the preparation of many lithium compounds. In recent years interest in lithium compounds has greatly increased, and this has resulted in the development of several new processes for the production of lithium hydroxide.

A widely used process is the causticization of lithium carbonate with lime.[3] The reaction proceeds according to the equation:

$$Li_2CO_3 + Ca(OH)_2 \rightarrow 2LiOH + CaCO_3\downarrow$$

The reactants are slurried together and boiled by means of steam. With 5% excess of slaked lime present and sufficient water to give a final concentration of 0•3lb. of lithium hydroxide per gallon, the conversion is nearly complete. The precipitated chalk is allowed to settle and the lithium hydroxide solution decanted. The solution is then evaporated and on cooling yields crystals of lithium hydroxide monohydrate.

The process described produces approximately 1 ton daily of lithium hydroxide monohydrate of 99% or greater purity. The plant is constructed in stainless steel. The major impurity in the product is lithium carbonate formed by the absorption of carbon dioxide from the atmosphere. Care is taken to exclude air wherever possible. The main disadvantage of the process appears to be the use of lithium carbonate as a starting material, which itself is the end product of a lengthy extraction process.

Lithium may be extracted direct from certain minerals as lithium hydroxide solution.

Spodumene ($Li_2O,Al_2O_3,4SiO_2$) is heated to 1100°C.[4] At this temperature β-spodumene is formed almost instantaneously and can be readily crushed to 200 mesh. The finely ground mineral, slaked lime and water are mixed in the ratio 1:2:5 and digested at 200°C. for 2hr. in an autoclave. The filtrate, dilute lithium hydroxide solution, contains approximately 85% of the lithium present.

A similar process is described[5] for the treatment of alkali aluminium silicates of the approximate composition SiO_2 50%; Al_2O_3 30%; Na_2O, K_2O, and Li_2O combined 15–20%.

Lithium hydroxide may also be extracted from spodumene by heating with lime and leaching with water.[4] Spodumene is converted to β-spodumene and finely ground. It is then mixed with 2·7 times its weight of finely ground limestone and heated to 1100°C. The sinter is reground and leached with boiling water. Up to 90% of the lithium present in the mineral is thus extracted as lithium hydroxide.

Petalite ($Li_2O,Al_2O_3,8SiO_2$) may also be treated in this way.

Physical Properties

Anhydrous lithium hydroxide crystallises in the tetragonal system,[6] the crystal parameters being a = 3·55A., c = 4·34A.

The unit cell consists of two molecules with Li^+ at 000 and ½½0 and OH^- at 0½u and ½0$\bar{u}$. The lattice parameter u = 0·20.

The lattice energy of the anhydrous salt calculated from the structure is 205kg.-cal./mole.[7]

When lithium hydroxide solutions are crystallized at room temperature lithium hydroxide monohydrate is produced. This salt crystallizes in the monoclinic system. Using Cu $K\,\alpha$-radiation[8] the axial ratios were found to be: a = 7·37A., b = 8·26A., c = 3·19A. The angle of inclination of 3rd. axis (β) = 110° 18′. The unit cell consists of four molecules, each Li^+ being at the centre of a tetrahedron of O^{--}. Two such tetrahedra share an edge in a reflection plane at an angle to the a axis Upper and lower corners of all tetrahedra are shared with tetrahedra in the cells immediately above and below, the edges between these shared corners being parallel to the c axis. Thus paired tetrahedra form unending chains in the c direction. O^{--} of the shared tetrahedral edges in the reflection planes are in OH^- groups and O^{--} in upper and lower tetrahedra are linked sideways by OH^- bonding between hydroxyl groups and water.

The scattering of light in hydroxide crystals in relation to the hydrogen bond has been studied spectrographically.[9] Light from a mercury vapour lamp is filtered, concentrated on the microcrystalline sample by means of a quartz condenser and projected on the spectrograph. Sharp lines for several hydroxides including anhydrous lithium hydroxide indicate no hydrogen bonding. A small increase in band width for the monohydrate indicated weak hydrogen bonding.

The density of lithium hydroxide monohydrate is 1·51g./c.c.[8]

The surface tension, density, viscosity and vapour pressure of aqueous solutions of lithium hydroxide are given in Tables I, II, III and IV.

TABLE I.- SURFACE TENSION OF AQUEOUS LITHIUM HYDROXIDE[10]

Concentration	Surface Tension (20°C.)
4·089N.	77·9 dynes/cm.
3·22	77·4
2·09	75·8
1·018	74·2

TABLE II.- DENSITY OF AQUEOUS SOLUTIONS OF LITHIUM HYDROXIDE[11]

Concentration	20°C.	30°C.	40°C.
0·5N.	1·0113	1·0087	1·0053
1·0	1·0242	1·0212	1·0178
2·0	1·0483	1·0451	1·0415
3·0	1·0703	1·0671	1·0634
4·0	1·0914	1·0880	1·0843
5·0	1·1117	1·1082	1·1049

TABLE III.- VISCOSITY OF AQUEOUS SOLUTIONS OF LITHIUM HYDROXIDE IN CENTIPOISES[11]

Concentration	20°C.	30°C.	40°C.
0·5N.	1·139	0·907	0·743
1·0	1·294	1·028	0·841
2·0	1·686	1·325	1·069
3·0	2·223	1·720	1·368
4·0	2·990	2·255	1·758
5·0	4·084	3·008	2·305

TABLE IV.- VAPOUR PRESSURE OF AQUEOUS LITHIUM HYDROXIDE[12]

Concentration (moles water per mole solute)	Vapour Pressure (mm.Hg)	
	0°C.	10°C.
10·83	3·85	7·44
13·30	3·99	8·02
17·10	4·12	8·29
22·37	4·24	8·54
44·52	4·40	8·86
∞	4·57	9·20

Neutron capture by aqueous lithium hydroxide has been calculated from results obtained with boric acid solutions.[13] A radium-beryllium source is placed at the centre of a glass balloon containing first distilled water and then lithium hydroxide solution. The neutron density is determined as a function of the distance from the centre, and the difference is due to neutron capture by lithium.

The ratio of cross sections for neutron capture thus determined is σ_{Li}/σ_H = 185.

Lithium hydroxide monohydrate is readily decomposed by heat to yield the anhydrous salt. A dehydration study[14] has shown that no fractional hydrate exists between $LiOH,H_2O$ and LiOH.

The melting point has been reported as 462°C.[15] and 471·3°C.[16] The salt has also been reported to show polymorphism, the transition from the α to the β form taking place at 413°C.[15]

The equilibrium $2LiOH(s) \rightleftharpoons Li_2O(s) + H_2O(g)$ has been studied by dynamic diffusion[17] and by both transpiration and effusion methods.[18] Water vapour pressures obtained by the transpiration method (passing nitrogen over a heated sample) and the effusion method (water vapour being pumped off from a heated sample) are in good agreement: selected values are given in Table V.

These figures are approximately one hundred times greater than those obtained by the dynamic diffusion method and as yet this discrepancy is unexplained. Comparison of the values obtained from these figures and those calculated from the Third Law of Entropies show close agreement:-

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	Experimental	Calculated
ΔH°	32·6kg.-cal.	32·8
ΔF°	22·5kg.-cal.	22·7
ΔS°	33·7 E.U.	33·85

TABLE V.- VAPOUR PRESSURE OF LITHIUM HYDROXIDE

Temp. (°K.)	Pressure (atm. × 10^7)
533	7·03
557	35·4
589	135·0
598	231·0
619	505·0
620	531·0
621	648·0

When introduced as an aqueous spray into an hydrogen-air flame, which could be made either oxidising or reducing, lithium hydroxide is reported to be stable up to 2300°K.[19]

Under these conditions the intensity of the resonance radiation emitted has been measured.[20] Lithium hydroxide was found to be the most stable of the alkali hydroxides and from the results obtained the collision diameter of the excited alkali atoms was calculated as $\sigma_{\mathrm{Li}}^2 = 22 \times 10^{-16}$ cm.^{2}.

The specific heat of a solution of 1 gram molecule of lithium hydroxide in 100 gram molecules of water is given as 0·9813.[21] The temperature coefficient of the specific heat is reported to be very small.

The heat of dilution of lithium hydroxide is reported as:-[21]

$\mathrm{LiOH,25H_2O} \quad + \quad \mathrm{25H_2O} \quad + 133$g.-cal.
$\mathrm{LiOH,25H_2O} \quad + \quad \mathrm{75H_2O} \quad + 223$g.-cal.
$\mathrm{LiOH,25H_2O} \quad + \mathrm{175H_2O} \quad + 288$g.-cal.
$\mathrm{LiOH,25H_2O} \quad + \mathrm{375H_2O} \quad + 338$g.-cal.
$\mathrm{LiOH,25H_2O}$ to infinite dilution $+ 390$g.-cal.

The work of dilution is given as:-[12]

Moles water per mole solute.	A°_{0}, g.-cal.	A°_{10}, g.-cal.
10·83	95	97
13·30	75	77
17·10	57	59
22·37	41	42
44·52	21	21
∞	0	0

The heat of neutralisation of lithium hydroxide[21] has been studied with a series of strong acids and strong bases at various concentrations. Extrapolation of the curves obtained to infinite dilution gave the value for the formation of water from $\mathrm{OH^-}$ and $\mathrm{H^+}$. In all cases an almost constant value of $\Delta H = -13{,}693$ g.-cal./mole was obtained.

The apparent molar heat capacity (Φ_C)[22] for lithium hydroxide is found to be $\Phi_C = -19{\cdot}98 + 12{\cdot}53m^{\frac{1}{2}}$ where m = molality of the solution, while $\bar{C}p_2$, the partial molar heat capacity of the solution, $= -19{\cdot}98 + 18{\cdot}80m^{\frac{1}{2}}$. These results agree fairly well with those of Richards and Rowe[21] who express some doubt regarding the purity of the lithium hydroxide used.

Experimental data have been summarized[23] and the following generalizations have been reached.

Φ_C is a linear function of $m^{\frac{1}{2}}$ for aqueous solutions of univalent strong electrolytes from infinite dilution to approximately $m = 2{\cdot}5$.

$\bar{C}p_2$ is a linear function of $m^{\frac{1}{2}}$. These relations are expressed by formulae:

$$\Phi_c = \Phi_c^\circ + Am^{\frac{1}{2}}$$

$$\bar{C}p_2 = \bar{C}p_2^\circ + \tfrac{3}{2}Am^{\frac{1}{2}}$$

$$\Phi_c^\circ = \bar{C}p_2^\circ$$

Over the range 18–25°C., A is constant at 17·9. At 25°C. $\Phi_c^\circ = -21{\cdot}6$, and $d\Phi_c^\circ/dT = \tfrac{2}{7}$ per degree. The heat capacity of a given solution in g.-cal. per gram of solution is given by

$$\bar{C}_p = \frac{1000 + m}{1000 + m\,M}$$

(where M = molecular weight of solute).

Heat content data for aqueous solutions of lithium hydroxide have been converted to 18°C. and tabulated.[24] The extrapolation to infinite dilution is made by employing the Debye–Hückel theory of strong electrolytes. Typical results are given in Table VI where $\Phi_h - \Phi_h^\circ$ = the relative apparent heat content of the solute, and $\bar{H}_2 - \bar{H}_2^\circ$ = the relative partial molal heat content of the solute.

TABLE VI.- HEAT CONTENT DATA FOR AQUEOUS SOLUTIONS OF LITHIUM HYDROXIDE

Moles solute per 1000 grams H_2O	$\Phi_h - \Phi_h^\circ$ g.-cal. per mole solute	$\bar{H}_2 - \bar{H}_2^\circ$ g.-cal. per mole solute
0	0	0
0·01	42	63
0·04	82	119
0·09	118	168
0·16	150	212
0·25	180	252
0·36	208	286
0·64	258	360
1·00	310	440
1·44	362	525
1·96	418	615

Heat capacities of solid lithium hydroxide and lithium hydroxide monohydrate have been measured between 15 and 300°K.[25] Integration of the heat capacity curves gives the molal entropy values at 298·16°K.

LiOH	10·23 ± 0·05 E.U.
$LiOH,H_2O$	17·07 ± 0·05 E.U.

The change in entropy at 25°C. for the reaction $LiOH,H_2O$ (cryst.) → LiOH (cryst.) + H_2O (liquid) obtained by Ueda[26] from data for the dissociation pressures of the hydrate and the heats of solution of the two crystals, combined with the value 10,520±3g.-cal. for the molal heat of vaporisation of water, is in good agreement with the ΔS_{25}° values[25] for the reaction $LiOH,H_2O$ (cryst.) → LiOH (cryst.) + H_2O (gas) computed from experimental entropy values and the entropy of steam. This demonstrates the applicability of the third law of entropies to lithium hydroxide.

$LiOH,H_2O$ (cryst.) → LiOH (cryst.) + H_2O (liquid)

$\Delta H_{25}^\circ = 4{,}020 \pm 20$g.-cal.

$LiOH,H_2O$ (cryst.) → LiOH (cryst.) + H_2O (gas)

$\Delta H_{25}^\circ = 14{,}540 \pm 23$g.-cal.

Heats of formation [27] are:-

$$\text{LiOH } \Delta H^\circ_{25} \; -116{,}589 \pm 90\text{g.-cal./mole.}$$
$$\text{LiOH,H}_2\text{O } \Delta H^\circ_{25} \; -188{,}926 \pm 120\text{g.-cal./mole.}$$

Free energies of formation[27] are:-

$$\text{LiOH } \Delta F^\circ_{25} \; -105{,}676 \pm 130\text{g.-cal./mole}$$
$$\text{LiOH,H}_2\text{O } \Delta F^\circ_{25} \; -163{,}437 \pm 160\text{g.-cal./mole.}$$

The high temperature heat content and entropy of lithium hydroxide has been determined up to 900°K.[16] Samples were sealed in gold capsules and the determinations carried out in a drop calorimeter. The following equations were derived to fit the experimental results:-

LiOH (cryst.) (400 – 744·3°K.)

$$H_T - H_{298\cdot16} = 11\cdot988\,T + 0\cdot00412\,T^2 + 226{,}700\,T^{-1} - 4701\text{g.-cal.}$$
$$S_T - S_{298\cdot16} = 27\cdot603 \log T + 0\cdot00824\,T + 113{,}350\,T^{-2} - 72\cdot035 \text{ E.U.}$$

LiOH (liquid) (744·3 – 900°K.)

$$H_T - H_{298\cdot16} = 20\cdot74\,T - 3638\text{g.-cal.}$$
$$S_T - S_{298\cdot16} = 47\cdot76 \log T - 116\cdot859 \text{ E.U.}$$

The heat of fusion at 744·3°K. = 5010g.-cal./mole.

The electrical conductance of aqueous lithium hydroxide solutions at 25°C. has been studied.[28] Over the concentration range 0·02703 moles/kg. of water to 0·001394 moles/kg. of water, the equivalent conductivity (Λ_C) rises from 223·1 to 232·5. A limiting value of 234·7 (Λ_0) is quoted. Later work[29] gives the limiting value as 237·2. Lithium hydroxide even at low concentrations appears to show considerable deviation from complete ionisation.

The conductance of certain non-aqueous solutions of lithium hydroxide is given in Table VII.[30,31]

TABLE VII.- CONDUCTANCE OF ALCOHOLIC SOLUTIONS OF LITHIUM HYDROXIDE

Litres solvent containing 1 gram molecule of solute	Molecular Conductivity		
	CH_3OH	C_2H_5OH	C_3H_7OH
2	24·35	-	-
4	34·15	7·2	-
8	42·83	9·45	-
16	50·92	12·0	-
32	58·32	15·35	4·15
64	64·96	18·3	5·33
128	70·25	22·0	6·8
256	74·45	25·4	8·52
512	77·69	28·11	-
	90·42	36·9	14·91

The *E.M.F.* was measured in the following cells.[32]

Pt. H_2 / LiOH / LiCl / AgCl / Ag
Pt. H_2 / LiOH / LiBr / AgBr / Ag

Combined figures gave the following values of dissociation constants for concentrations up to an ionic strength of 0·1.

Temperature	Dissociation Constant
5°C.	0·55 ± 0·02
15°C.	0·64 ± 0·02
25°C.	0·66 ± 0·02
35°C.	0·63 ± 0·01
45°C.	0·65 ± 0·02

The spectral absorption of lithium hydroxide solutions of various concentrations has been determined.[82] Results over the range 1–3μ were compared with those of water and all curves showed a broad intense absorption band with a maximum at 2·29μ. This band was thought to be due to dissociated hydroxyl ions. Maximum absorption with water was observed at 1·48μ and 1·98μ. The effect of dissolving lithium hydroxide was to decrease the absorption of the band at 1·48μ by an amount proportional to the concentration of the solution.

Later workers[83,84] confirmed this work by finding a maximum at 2·30μ but discovered that the position of the water maximum changed in the presence of alkali. Alcohol solutions of alkalis were therefore studied and in all cases small bands occurred at 0·96μ 1·10μ and 1·27μ which were attributed to hydroxyl ions.

Solid Systems Containing Lithium Hydroxide.

Li, K || OH, Cl[33]

The binary system LiOH–KOH forms an incongruent melting compound, 2LiOH,KOH, which forms solid solutions with KOH with a minimum melting point of 227°C.

The system LiCl–KCl forms a eutectic at 325°C. containing 43 mole % KCl. In the system LiOH–LiCl a 1 : 1 compound is formed which gives with LiOH a eutectic melting at 262°C. and containing 37 mole % LiCl.

The equilibrium KOH + LiCl $\rightleftharpoons$ LiOH + KCl is shifted strongly in favour of LiOH-KCl. The diagonal section LiOH-KCl is stable.

The six invariant points are:-

Temp. °C.	Mole %				Solid Phases
	LiOH	KOH	LiCl	KCl	
Eutectic 228	30·0	64·0	-	6·0	γ-KOH, KCl, 2LiOH,KOH
Eutectic 280	43·5	-	45·0	11·5	LiCl, KCl, LiOH,LiCl
Eutectic 283	62·0	-	36·5	1·5	LiOH, KCl, LiOH,LiCl
Transition 311	58·5	38·5	-	3·0	LiOH, KCl, 2LiOH,KOH
Transition 310	21·0	69·5	-	9·5	β-KOH, KCl, 2KOH,KCl
Transition 347	22·0	65·0	-	13·0	2KOH,KCl, KCl, KOH,KCl

Li, K || OH, CrO_4[34]

In this system the equilibrium is strongly shifted in the direction of the more stable pair LiOH–K_2CrO_4.

In the binary system Li_2CrO_4–K_2CrO_4 there is a compound Li_2CrO_4,K_2CrO_4 m.p. 550°C., and eutectics containing 74 mole % Li_2CrO_4 m.p. 415°C. and 46 mole % Li_2CrO_4 m.p. 546°C.

In the binary system LiOH–Li_2CrO_4 there are two compounds, 4LiOH, 3Li_2CrO_4 m.p. 430°C. and LiOH,Li_2CrO_4 m.p. 460°C.; also three eutectics containing 45 mole % Li_2CrO_4 m.p. 318°C., 64 mole % Li_2CrO_4 m.p. 427°C. and 78 mole % Li_2CrO_4 m.p. 450°C. The system LiOH–K_2CrO_4 is stable and represents a quasibinary system with a eutectic at 3·5 mole % K_2CrO_4 m.p. 468°C.

In the stable triangle LiOH–Li_2CrO_4–K_2CrO_4 there are three compounds, 4LiOH,3Li_2CrO_4, LiOH,Li_2CrO_4 and Li_2CrO_4,K_2CrO_4 and four invariant points which are.

Temp. °C.	Mole %		
	LiOH	Li_2CrO_4	K_2CrO_4
Eutectic 339	47·0	43·0	10·0
Eutectic 378	17·5	63·5	19·0
Transition 373	52·5	33·5	14·0
Transition 369	35·0	52·0	13·0

In the stable triangle LiOH–KOH–K_2CrO_4 there is a field of the compound

2LiOH,KOH and two invariant points.

Temp. °C.	Mole % KOH	Mole % LiOH	Mole % K_2CrO_4
Eutectic 200	69·0	25·0	6·0
Transition 335	38·0	60·0	2·0

Li, Na || OH, CrO_4[35]

The reaction of the system may be expressed by $2NaOH + Li_2CrO_4 \rightleftharpoons 2LiOH + Na_2CrO_4$ with the equilibrium shifted towards the more stable pair $NaOH$-Li_2CrO_4.

In the binary system NaOH-LiOH there are three transition points at 254, 238 and 299°C. with 57·0, 61·5 and 94·5 mole % NaOH. Two compounds of uncertain compositions are formed. The binary system $LiOH$-Li_2CrO_4 behaves as in the previous system.

In the stable triangle $LiOH$-$NaOH$-Na_2CrO_4 there are three fields of crystallization: LiOH,NaOH, $4NaOH,Na_2CrO_4$, and $2NaOH,Na_2CrO_4$. There are three transition points at 228, 270 and 304°C. and a eutectic at 221°C.

In the stable triangle $LiOH$-Li_2CrO_4-Na_2CrO_4 there are six fields of crystallisation, $4LiOH,3Li_2CrO_4$, $LiOH,Li_2CrO_4$, Li_2CrO_4,Na_2CrO_4, $4LiOH,Na_2CrO_4,3Li_2CrO_4$, and two polymorphic forms of Li_2CrO_4.

Li, K || OH, Br.[36]

This system has nine fields of crystallisation including the pure components and the compounds 2LiOH,LiBr and 2LiOH,KOH.

Li, K || OH, NO_3.[37]

The binary system $LiOH$-$LiNO_3$ has a eutectic at 40·5 mole % LiOH with m.p. 183°C. There is a compound $LiOH,LiNO_3$ decomposing at 195°C. The system has ten fields of crystallisation including the pure components and the compounds 2LiOH,KOH and $LiOH,LiNO_3$.

Liquid Systems Containing Lithium Hydroxide.

The solubility curve for lithium hydroxide in aqueous sodium hydroxide shows a minimum at 12·7N-NaOH as illustrated in Table VIII. Below this concentration the solid phase is $LiOH,H_2O$ and above it is LiOH.

TABLE VIII.- SOLUBILITY OF LITHIUM HYDROXIDE IN AQUEOUS SODIUM HYDROXIDE SOLUTIONS

Concn. of NaOH (Normality)	Solubility g. Li_2O/100g. solution
8·0	1·352
10·1	0·913
12·1	0·574
12·7	0·474
14·6	0·613
18·4	0·726
19·7	0·787

The equilibrium between aqueous lithium hydroxide and solvents normally completely miscible with water has been studied.[39,40] Organic liquids studied include pyridine, dioxan and acetone. Equilibrium concentrations for the dioxan system are given in Table IX.

TABLE IX.- SOLUBILITY OF LITHIUM HYDROXIDE IN AQUEOUS DIOXAN

LiOH (pts./wt.)	H_2O (pts./wt.)	Dioxan (pts./wt.)
12·25	87·75	-
5·63	86·35	8·02

continued on following page

TABLE IX (continued)

LiOH (pts./wt.)	H_2O (pts./wt.)	Dioxan (pts./wt.)
2·41	76·37	21·22
1·04	67·16	31·80
0·33	43·37	56·30
0·05	16·20	83·75
-	-	100

Chemical Properties

The general chemistry of lithium hydroxide is well established. Reactions recently studied are summarised below:

In the reaction between nascent chlorous acid and lithium hydroxide,[41] an aqueous solution of chlorine dioxide, together with twice the stoicheiometric quantity of hydrogen peroxide, is added to a lithium hydroxide solution at 20°C. and the solution is allowed to remain at this temperature for 5hr. The main product is lithium chlorite, although considerable quantities of lithium chlorate are also formed.

Lithium hydroxide reacts in the cold with phosphoric acid to give either insoluble Li_3PO_4 or LiH_2PO_4, depending on the ratio of lithia to phosphate. Di-lithium hydrogen phosphate is not formed. Neither of the known salts is hydrated.[42,43]

Lithium hydroxide reacts with nitric oxide according to the following equations:[44]

$$2LiOH + 4NO \rightarrow N_2O + 2LiNO_2 + H_2O$$
$$4LiOH + 6NO \rightarrow N_2 + 4LiNO_2 + 2H_2O.$$

The reaction at room temperature is extremely slow and produces essentially lithium nitrite and nitrous oxide containing a little nitrogen. It is estimated that several years would be required for the reaction to go to completion. Rise of temperature greatly accelerates the reaction. At 280°C. the second reaction assumes greater importance, approximately 25% of nitrogen being found in the nitrous oxide. At this temperature the reaction goes to completion in approximately 24hr. Above 280°C. the study of the reaction is complicated by the decomposition of lithium nitrite.

Lithium hydroxide solutions react with freshly prepared gallium hydroxide.[45] If excess of gallium hydroxide is added to the boiling alkali solution, after filtration and evaporation hexagonal plates of $Li_2O,Ga_2O_3,12H_2O$ separate. This compound loses water even at room temperature and may be readily dehydrated over sulphuric acid or by gentle heating to give $Li_2O,Ga_2O_3,2H_2O$. Strong heating results in the formation of $LiGaO_2$.

The reaction of aqueous lithium hydroxide with arsenious oxide at 25°C. gives only $LiAsO_2$.[46]

Aqueous solutions of lithium hydroxide and boric acid react, depending on their ratio, to give the following salts:-[47,48]

$$Li_2O,5B_2O_3,10H_2O$$

stable above 40·5°C.

$$Li_2O,2B_2O_3,3H_2O$$

formed from a solution of the above salt below 40·5°C. or directly. Stable over the range 0–100°C.

$LiBO_2,8H_2O$ - stable below 36–9°C.
$LiBO_2,2H_2O$ - stable above 36–9°C.

Several reactions of lithium hydroxide with non-metals have been studied.[49]

Heating lithium hydroxide with sulphur gives hydrogen sulphide, lithium sulphide, lithium sulphite and lithium sulphate. Heating with selenium gives hydrogen selenide, lithium selenide and lithium selenate. With red phosphorus the products are phosphine and lithium phosphate. Mixtures of lithium hydroxide with sulphur, selenium or phosphorus are capable of reducing nitrates or nitrocompounds to ammonia.

The reaction of inorganic bases and tertiary amyl halides with lithium hydroxide has been studied.[50] The formation of the corresponding olefin increases with temperature and with hydroxide concentration. At 45°C., using lithium hydroxide, *tert.*amyl chloride gave a 17% yield of olefin.

The behaviour of lithium hydroxide towards trimeric phenylstibinic acid, $[(3\text{Ph SbO}_2)\text{ H}_2\text{O}],n\text{H}_2\text{O}$, differs from that of sodium and potassium hydroxides.[51] The trimeric acid and its amino derivative are neutralised by 3 molecules of sodium or potassium hydroxide to give the salts of its monomer. Lithium hydroxide however neutralises only 1 molecule giving probably the salt of the monomer and excess acid in a dimeric form. Other substitution products are completely neutralised by all three alkalis.

In preparing glycylglycine,[52] the yield is markedly improved by substituting lithium hydroxide for sodium hydroxide.

In the base-catalysed reaction between phenol and formaldehyde[53] the rate of reaction is found to be less in the presence of lithium hydroxide than with sodium, potassium or barium hydroxides. This is thought to be due to the greater hydration of the lithium ion.

Two reactions of lithium hydroxide with citral have been studied polarographically:[54]

(i) decomposition with lithium hydroxide results in the formation of acetaldehyde and methylheptenone by cleavage.

(ii) lithium hydroxide catalyses the condensation of citral and acetone to pseudoionone.

Applications

Lithium hydroxide is manufactured on a very large scale and is widely used as a raw material for producing other lithium compounds.

It has found considerable application as an absorbent for gases and water vapour. A patent describes a preparation[55] where lithium hydroxide monohydrate is mixed with 20% of its weight of 20% sodium silicate solution. The mixture is moulded as required and heated to drive off water. The resulting mass, which is porous and does not become gummy in use, is capable of absorbing 76% of its weight of carbon dioxide in two hours. A similar preparation is described for use in submarines.[56] Lithium hydroxide has the advantage that carbon dioxide is removed readily from air at temperatures as low as −30°F. It is also used in submarines and ventilating systems in conjunction with sodium peroxide for the regeneration of respired air.[57] The constituents are ground together, a little water is added and the mixture compressed. After heating to expel water, the hard porous mass may be crushed to size. Two satisfactory mixtures are:

Na_2O_2	40 (parts by weight)	Na_2O_2	65
$LiOH,H_2O$	9	$LiOH,H_2O$	9½
$CuOCl_2$	½	$Ca(OH)_2$	1
		NiO	½

Lithium hydroxide behaves similarly to sodium hydroxide in the mercerization and xanthation of cotton fibres. It therefore finds some application in this field where limited variations in conditions and properties are required. The subject has been widely investigated.[58,59,60] It has been shown that while alkalis other than lithium hydroxide give addition compounds with cellulose in a stoicheiometric ratio,[61-64] no definite compounds with lithium hydroxide are observed. Of the alkalis, lithium hydroxide causes the greatest swelling.[65] Cellulose mercerized with lithium hydroxide may be xanthated in much the same way as with sodium hydroxide. Xanthates so formed however are not completely soluble in alkali.[66]

Lithium hydroxide when chlorinated yields lithium hypochlorite, which is a good textile bleach.[67] It can be purified and stored in the crystalline state without deterioration.

Lithium hydroxide is sometimes used in the tanning of hide.[68] It is absorbed to a greater extent than other alkalis, but causes less swelling.

Silica sols may be stabilized with lithium hydroxide[69] added as a solution to the sol in the molar ratio SiO_2:LiOH 5:1. The mixture immediately sets to a firm gel, which disperses spontaneously to a fluid sol after 17hr. Such sols are used in the preparation of catalysts, phosphors and phosphor adhesives and also in the treatment of leather, paper and textiles.

Lithium hydroxide is a usual additive to the electrolyte of alkaline storage batteries. The efficiency of a battery of this type decreases with the life of the nickel anode. By adding lithium hydroxide to the potassium hydroxide it is possible to increase the anode capacity by 40% for a given cell (50g. of lithium hydroxide per litre gives an increase of approximately 22%).[70] This is thought to be due to the increase in oxygen overvoltage caused.[71,72] The carbonate concentration of the electrolyte is maintained substantially lower by the deposition of insoluble lithium carbonate.[73]

Additions of lithium hydroxide to cracking catalysts are often made to alter their selectivity.[74] A silica-alumina catalyst of composition SiO_2 89·5% Al_2O_3 10·0% and H_2O 0·5% may be rendered inactive for the cracking of hexadecane by the addition of lithium hydroxide. The same addition however renders it more active for the cracking of di-*iso*butylene. A high proportion of its activity for cracking cumene is retained after the lithium hydroxide treatment. A similar effect is observed with catalysts for cracking cetane.[75] It is thought that lithium hydroxide and other alkalis neutralise different acidic active sites effective in the cracking of hydrocarbons.

Alloys of the type Al 40%, Cu 55%, Zn 5% or Al 40%, Cu 50%, Zn 5%, Ni 5% are treated with strong aqueous alkalis to give Raney type catalysts.[76] Aluminium dissolves and the granular powders formed readily dehydrogenate *cyclo*hexanol to *cyclo*hexanone, but are inactive in the dehydration of *cyclo*hexanol to *cyclo*hexene. Preparation by means of lithium hydroxide gives catalysts active for both reactions.

Short chain hydrocarbons may be synthesized from carbon monoxide and hydrogen using supported iron catalysts.[77] A solution of ferrous chloride is added to a lithium carbonate slurry prepared *in situ* from lithium hydroxide and ammonium carbonate, further ammonium carbonate is added and the mass washed free from chloride.

Lithium hydroxide may be used as an alternative to potassium hydroxide in the alkali activated production of water gas from steam and coal.[78]

The crevice corrosion of stainless steel couples in water up to 600°F. has been investigated.[79] The formation of iron oxide was retarded by small additions of lithium hydroxide to the water.

Wax type esters may often be solubilised by means of their metal soaplike reaction products.[80] These can readily be dissolved in normal solvents to form varnishes, lacquers etc. Lithium hydroxide and Japan wax are cited as an example.

A preparation[81] for the manufacture of porous cement has been patented. A slurry containing lithium hydroxide, casein and bentonite is added in small quantities to the cement mixture.

Analytical

A 1% lithium hydroxide solution containing 5% of potassium nitrate may be used as a substitute for yellow ammonium sulphide in the separation of the copper and arsenic groups.[85] The sulphides of arsenic, antimony and tin readily dissolve while those of the copper group are insoluble, though mercuric sulphide begins to dissolve slowly on boiling. The reagent is cheaper and more pleasant to use than yellow ammonium sulphide.

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SECTION IX

LITHIUM PEROXIDE

By R.E. OLIVER

PREPARATION AND FORMATION

A small-scale preparation of lithium peroxide is described[1] in which $Li_2O_2,H_2O_2,2H_2O$ is prepared as an intermediate compound. Lithium metal (2 g.) is dissolved in absolute alcohol (250 ml.). Lithium ethoxide, which separates, is filtered and washed with absolute alcohol. The ethoxide is then suspended in absolute alcohol (250 ml.) and treated with 30% hydrogen peroxide (25 ml.). After stirring for several hours the mixture is filtered in a carbon-dioxide-free atmosphere. A 56% yield of $Li_2O_2,H_2O_2,2H_2O$ results, which is dehydrated over phosphorus pentoxide at 20 mm. pressure, to give lithium peroxide.

A similar preparation is described in a recent patent.[2] A lithoxy-compound such as an alcoholate, is treated with the stoichiometric proportion of aqueous hydrogen peroxide. An organic liquid such as propyl or allyl alcohol forming an azeotropic mixture with water is added, and the mixture distilled. It is claimed that a 95% recovery of almost pure lithium peroxide is obtained by filtration of the residual organic phase.

Lithium peroxide is formed in considerable quantities in the course of a number of reactions. Anhydrous lithium nitrate[3] is added to liquid ammonia contained in a trap cooled in solid carbon dioxide. A sodium superoxide is added, and the mixture stirred while the ammonia is allowed to evaporate. Reactions of the type:

$$LiNO_3 + NaO_2 \rightarrow Li_2O_2 \text{ (35\% yield)}$$
$$LiNO_3 + 2NaO_3 \rightarrow Li_2O_2 \text{ (29\% yield)}$$

occur; by-products, including the normal oxide, amide, nitrite and hydroxide, are also formed.

Lithium metal may be dissolved in liquid ammonia[4] to give a blue solution. If oxygen is passed through the solution is becomes colourless. On evaporating the ammonia a residue containing 23% of Li_2O_2 and 77% of Li_2O remains.

The action of oxygen on lithium amalgam gives a mixture containing approximately 30% of Li_2O_2 and 70% of Li_2O.[5]

PHYSICAL AND CHEMICAL PROPERTIES

Until recently it was thought that lithium peroxide crystallized in the tetragonal system.[1,6,7] The most recent investigations[8] have shown it to be hexagonal, with $a = 6{\cdot}305$ A., $c = 7{\cdot}710$ A. The unit cell contains 8 molecules.

The density of lithium peroxide has been determined.

2·26 g./c.c. at 25°C.[1]
2·297 g./c.c. at 25°C.[8]

The melting point has also been determined:

425°C.[9]
460°C.[10]

Lithium peroxide is unstable under normal conditions of temperature and pressure, but may be kept for short periods at low temperatures in the absence of light.[1]

The dissociation temperature (760 mm.) is 195°C.[9] The dissociation pressures (Table I.) of lithium peroxide at various temperatures have been determined by a dynamic method.[10]

TABLE I.- DISSOCIATION PRESSURES OF LITHIUM PEROXIDE

Temp. °C.	*p* (mm.)
43	5
54	12
87	47
93	66
116	122
127	184
148	271
181	497
198	790

The heat of dissociation is +13·6 kg.-cal.[10] The heat of formation is +144·8 kg.-cal.[9] An *α* to *β* transformation is reported to take place at 225°C.[11]

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SECTION X

LITHIUM FLUORIDE

By A. B. TRENWITH

In the preparation of lithium fluoride interest has centred on the production of large single crystals from which optical components, particularly for infra-red apparatus, may be fabricated.

Two common procedures for synthesizing lithium fluoride are the neutralization of lithium bicarbonate solution by hydrofluoric acid[1] and the double decomposition between lithium chloride and ammonium fluoride solutions.[2,3]

Of the methods used for preparing crystals from the pure material that devised by Stockbarger,[1,5] involving slow cooling of the melt, produces satisfactory specimens, particularly when the operation is carried out in a vacuum furnace. Optical lithium fluoride has also been prepared by a procedure devised by Kyropoulos[4,5] in which crystallization is initiated by a crystal seed and the crystal is cooled at a very slow rate. Some modifications of the above procedures have been employed.[6,7] An investigation of the properties of synthetic lithium fluoride crystals[8] has shown that wide variations occur and that vacuum-grown crystals are generally the most suitable for use in optical systems. Traces of impurity in the lithium fluoride cause a marked deterioration in the optical properties of the final crystal. One method of purification[9] involves treatment of the powder with fluorine for long periods at elevated temperatures.

Lithium fluoride has a face-centred cubic lattice. The lattice constant determined by electron diffraction[10] is $a = 4{\cdot}015 \pm 0{\cdot}002$A. For crystal sizes of less than 100A. the lattice constant decreases slightly with crystal size. The internuclear distance and dipole moment determined by molecular beam spectroscopy[11] are 1·51A. and 6·6 Debye units respectively. Quantum mechanical computation of the lattice energy[12] gives a value of 239 kg.-cal./mole (as against the experimental value 240 kg.-cal./mole) and the surface energy of a (100) face at 0° abs. is found to be 557 ergs/sq.cm.[13]

The lithium-fluoride bond has a greater covalent character than any other alkali metal-fluoride bond; a value of 11% covalent character has to be introduced into calculations of binding energy, internuclear distance and dipole moment to bring the results into line with experimental data.[14]

The density of the solid fluoride determined by the temperature-of-flotation method[15] is $d_{25} = 2{\cdot}63905 \pm 0{\cdot}0001$ and the coefficient of linear expansion[15] up to 380° is $\alpha_t = 0{\cdot}0_4 3376 + 0{\cdot}0_7 2054t + 0{\cdot}0_{10} 4885t^2$. Owing to the suitability of lithium fluoride as a material for making optical windows and spectroscope prisms the optical properties for the ultra-violet and infra-red regions have been studied in detail.[16-20] Values obtained for the elastic constants by measurement of ultrasonic velocities[21] and by the study of reflexions of diffuse X-rays[22] show only fair agreement. In studying the effect of pressure on crystalline solids,[23] lithium fluoride was found to show no distortion up to 4000 kg./sq. cm.; it would therefore be a suitable material for optical windows in high pressure apparatus.

Determination of the refractive index of lithium fluoride at 21° in the visible region[24] yields $n_F = 1{\cdot}394810$; $n_D = 1{\cdot}392057$ and $n_C = 1{\cdot}390862$. The temperature variations of the refractive index measured between 0° and 400° for the wave-lengths 2537A., 3650A., 4358A., 5461A. and 5893A. are given in Table I.[25]

TABLE I.- TEMPERATURE VARIATIONS OF REFRACTIVE INDEX FOR LITHIUM FLUORIDE AT VARIOUS TEMPERATURES

Temp. °C.	$dn/dt \times 10^5$				
	2537A.	3650A.	4358A.	5461A.	5893A.
50	-1·10	-1·20	-1·25	-1·27	-1·27
100	-1·31	-1·37	-1·42	-1·44	-1·44
150	-1·45	-1·54	-1·60	-1·61	-1·60
200	-1·67	-1·75	-1·81	-1·81	-1·82
250	-2·00	-1·95	-2·01	-2·03	-2·03
300	-2·23	-2·20	-2·25	-2·26	-2·27
350	-2·44	-2·51	-2·56	-2·56	-2·58
400	-2·65	-2·78	-2·80	-2·82	-2·85

Taking the heat of formation of HF gas to be 65·0 kg.-cal., the heat of formation of lithium fluoride is 144·7 kg.-cal.[26] The Debye temperature drops steadily from 646 at 0°C. to 606 at –197·6°C. and then rises rapidly with further decrease in temperature, a value of 750 being obtained at –254·4°C.[26a] The heat content[27] from 0°C. to the m.p. (848°C.) is given by:-

$$H_t(\mathrm{s}) - H_0(\mathrm{s}) = 2{\cdot}26938t + 8{\cdot}6291(10^{-5})t^2 - 1{\cdot}01322(10^{-7})t^3 + 1{\cdot}6845(10^{-10})t^4 - 451{\cdot}849 \log\{(t + 273{\cdot}16)/273{\cdot}16\}$$

and from the melting point to 896°C. by:-

$$H_t(\mathrm{l}) - H_0(\mathrm{s}) = 657{\cdot}48 + 2{\cdot}50101t.$$

The standard entropy S°_{LiF} at 25°C. = 8·52 g.-cal./mol.

The heat of dissociation of lithium fluoride vapour determined by an optical method[28] is 78·4 ± 2·5 g.-cal. in comparison with the thermochemical value of 71·25 g.-cal.

The thermal conductivity of a single crystal[29] varies linearly with temperature over the range 100°–500°C., values of 0·00613 and 0·0138 g.-cal.sec.$^{-1}$ cm.$^{-2}$°C.$^{-1}$cm. being obtained at 105° and 499°C. respectively.

Electrical conductivity measurements[30] show that at the melting point a single crystal of lithium fluoride has a conductivity of $0{\cdot}6 \times 10^{-2}$ ohms^{-1}cm.$^{-1}$ Just below the melting point the conductivity varies exponentially with the reciprocal of the absolute temperature. Lithium fluoride crystals have a dielectric constant of 9·27 ± 0·02 at 20°C.,[31] the coefficient of temperature variation[32] being $3{\cdot}75 \times 10^{-4}$.

Of the binary systems containing lithium fluoride which have been studied those which form simple eutectics are recorded in Table II.

TABLE II.- BINARY SYSTEMS CONTAINING LITHIUM FLUORIDE WHICH FORM SIMPLE EUTECTICS

System	M.p. of eutectic (°C.)	Mole-% LiF	Ref.
LiF-MgF_2	{742	67	33
	{735	64	34
LiF-NaF	652	61	35
LiF-CaF_2	–	–	36
LiF-LiCl	484	30·5	37
LiF-Li_2CO_3	608	49	38
LiF-Li_2MoO_4	617	38	39
LiF-Li_2WO_4	642	38	39

In the system LiF–Li_2CrO_4 the compound Li_3CrO_4F is formed.[39] Another system giving rise to compound formation is LiF–BaF_2 which yields[37] $LiBaF_3$ also formed in the system LiF–BaO.[38] This compound which is cubic (a = 3·988A.) has an inverted perovskite structure and melts with decomposition at 850°C. The system LiF–AlF_3 yields Li_3AlF_6, m.p. 790°C.[39] On adding beryllium fluoride to lithium fluoride the temperature of crystallization is lowered, approaching the peritectic point at 461°C. and 38·5% BeF_2; at this temperature the compound Li_2BeF_4 is formed. With further increase in the concentration of beryllium fluoride the transition point is reached at 353°C. and 52·0% BeF_2 and as a result of the peritectic reaction the compound $LiBeF_3$ is formed; this compound is unstable, decomposing to yield Li_2BeF_4. A third compound $LiBe_2F_5$ corresponding to 66·7% BeF_2 decomposes at 277°C. without melting.[40,41] A thermal investigation of the system LiF–$LiBO_2$ indicates the formation of the compound $Li_3BO_2F_2$.[42] Evaporation of mixed solutions of lithium fluoride and aluminium fluoride yields colloidal solutions of the salt $Li_5Al_2F_8$.[43]

The crystal growth of lithium fluoride deposited from the vapour phase on various substrates has been examined by electron diffraction. On amorphous substrates[44] films thinner than 100A. showed completely random structure, but as the thickness increased the crystals showed a definite preferred orientation. A definite orientation was also observed on silver,[45] on other alkali halides,[46,47] on calcium carbonate,[48] on sodium nitrate[48] and on mica substrates.[49]

The heat and free energy of hydration of lithium fluoride are[50] 238 and[51] 219 kg.-cal. per mole respectively. It is the least soluble of the alkali metal fluorides, a fact attributable to the high lattice energy of the crystal. Its solubility in water increases over the temperature range 0°–35°C. from 0·1203 to 0·1354 g./100g. of water.[52] The solubility–temperature curve must reach a maximum between 35° and 198°C. since solubility measurements in the region 198°–375°C. show a decrease in solubility with increase in temperature from 0·1081 to 0·0222 g./100g. of solvent.[53] The solubility in water above its critical point remains practically constant with temperature at a solvent density of approx. 0·36. The solubility increases with temperature for higher densities and decreases with rising temperature for lower densities.[53]

Although only slightly soluble in water, lithium fluoride dissolves readily in liquid hydrogen fluoride. Over the temperature range −23° to 12°C. the solubility is virtually constant at 10·3g. LiF per 100g. HF.[54] The salt $LiHF_2$ formed in this system is unstable, losing hydrogen fluoride at room temperature in the solid state.[55] The formation and subsequent decomposition of $LiHF_2$ thus provides a means of preparing pure hydrogen fluoride.

The current–voltage curves for aqueous solutions of lithium fluoride at 25°C. show two breaks,[56,57] the first at 1·61V. and the second at 2·95V. The former is taken to correspond to the primary decomposition of water and the second is taken to be the decomposition potential of the salt.

Lithium fluoride is not hygroscopic and has a slight acid reaction; consequently it is a suitable material for use as a flux in a number of processes. It is used as a constituent of aluminium welding fluxes[58] and brazing fluxes for zirconium and titanium,[59] and as a fluxing agent in the sintering of such refractory materials as alumina, thoria and beryllium oxide,[60] magnesium-lithium alloys[61] and metallic beryllium.[62] Lithium fluoride is the most powerful known mineralizing agent in the mullitization process.[63]

Lithium fluoride has been used as a catalyst for the combined dehydrogenation and dehydration of ethyl alcohol. Dehydrogenation is the predominant reaction with this catalyst.[64] Other miscellaneous uses of lithium fluoride include the determination of cyclotron beam energies[65] by measurement of the depth of penetration of a yellow colour produced in a lithium fluoride crystal, and its use as a shadow-coating agent in electron microscopy.[66] The amount of light reflected from a glass surface may be reduced by coating with a thin suspension of finely ground lithium fluoride in a water-soluble organic solvent such as alcohol;[67] petroleum lubricating oils may be decolorized by contact with powdered lithium fluoride;[68] finely divided lithium fluoride has been found to be efficient in preventing explosions in methane-air mixtures;[69] the stability of boric oxide glasses is improved by adding 1 mole of lithium fluoride with each 0·5 to 10 moles of boric oxide;[70] lithium fluoride crystals have been used as *X*-ray crystal monochromators, an intense multiple reflexion being produced on exposing a natural cleavage surface to an *X*-ray beam.[71]

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SECTION XI

LITHIUM CHLORIDE

By R. E. OLIVER

PREPARATION AND PRODUCTION

Solutions of lithium chloride may be readily prepared in the laboratory by dissolving either the hydroxide or the carbonate in hydrochloric acid. Lithium chloride is also formed by the direct combination of the elements, or by the dissolution of the metal, oxide or silicate in hydrochloric acid. The anhydrous salt is obtained only with difficulty by evaporation of a solution, as the concentrated solutions are extremely corrosive and the anhydrous salt deliquescent.

Anhydrous lithium chloride may be prepared by solvent extraction with amyl alcohol. In one method described[200] a saturated aqueous solution of lithium chloride is treated with excess dioxan. Approximately half the lithium chloride separates as $LiCl,H_2O,(C_2H_4)_2O_2$. The solid is desolvated at reduced pressure, the temperature being raised gradually to 150°C. A residue of pure anhydrous lithium chloride remains.

Production from lithium carbonate is carried out on a large scale.[1] The damp carbonate containing approximately 8–12% of water is treated with hydrochloric acid in a rubber-lined vessel. The slightly acid solution (*d* 1·2) is freed from sulphate with barium chloride; excess acid is removed with lithium carbonate and barium with sulphuric acid. The solution is then made slightly alkaline with lithium hydroxide and evaporated. A solid lithium chloride containing only 1% of water is prepared by passing the solution down a ceramic tower against rising flue gases.

Patent specifications[2,3] describe a development of this technique whereby fused mixtures of lithium oxide and lithium chloride (present in practice as hydroxide or carbonate and near-anhydrous chloride) are passed down a heated tower against a chlorinating agent such as hydrogen chloride, carbon and chlorine, carbon monoxide and chlorine, or phosgene, to give the fused anhydrous chloride.

Many processes have been developed for the recovery of lithium chloride from minerals. In a process using spodumene[4] and similar lithium-containing silicates[5] the mineral is sintered with calcium sulphate and calcium carbonate for 2-3 hr. at 1100°C. The roasted product is cooled and leached with aqueous calcium chloride solution. Lithium, sodium and potassium dissolve as chlorides. Sulphate present in the solution is again removed with barium chloride, and barium and calcium with lithium carbonate. The solution is then evaporated; sodium and potassium chlorides are almost insoluble in concentrated lithium chloride solution and are precipitated. The final purification step, to remove the last traces of sodium and potassium, is to extract with hot 2-ethylhexanol, in which only lithium chloride is soluble, re-extract into water, and evaporate to dryness.

A patent process[6] describes the volatilization of lithium chloride from aluminosilicate minerals by heating with carbon in a stream of chlorine.

Another volatilization technique has been applied to minerals of the spodumene type.[7] 100 parts of calcined spodumene containing 1·2% of Li were ground to 200 mesh and mixed with 25 parts of anhydrous calcium chloride. The temperature was raised to 1050°C. and the pressure reduced to 5 mm. of mercury. Over a period of eleven hours the temperature was raised to 1150°C. and the pressure reduced to 2·5 mm. The condensate was estracedt with alcohol. A recovery of 96·5% of the lithium as lithium chloride is claimed. A similar process[9] describes the recovery of the lithium chloride by electrostatic precipitation.

Low-grade lithium minerals such as pegmatite ores containing 30% of spodumene may be concentrated by flotation and similarly treated.[8]

Lithium chloride may be recovered in high yield by volatilization from lepidolite.[10] The charge is heated to a temperature as near as practicable to the melting point of lepidolite (935°C.) and hydrogen chloride is passed over. A substantial excess of hydrogen chloride was found to be necessary, but a nearly theoretical recovery is claimed after 13 hr. Anhydrous lithium chloride was recovered from the cooler zones and a solution from the hydrochloric acid scrubbing towers.

Dilithium sodium phosphate, Li_2NaPO_4, is recovered as a by-product in the evaporation of liquors from Searles Lake, California. A patent specification[11] describes the conversion of this residue to lithium chloride. The salt is treated with slaked lime in an autoclave heated with steam at 100 lb. per sq. in. The reaction may be represented by the equation:-

$$2Li_2NaPO_4 + Ca(OH)_2 \rightarrow Li_4Ca(PO_4)_2\downarrow + 2NaOH.$$

The insoluble double calcium phosphate is filtered and washed. It is then treated with calcium chloride in an autoclave heated with steam at 50 lb. per sq. in.:-

$$Li_4Ca(PO_4)_2 + 2CaCl_2 \rightarrow 4LiCl + Ca_3(PO_4)_2\downarrow.$$

The lithium chloride solution is separated by filtration.

A patent specification describes the treatment of lithium-containing ores with hydrofluosilicic acid.[12] A water-soluble salt, Li_2SiF_6, is formed, which is decomposed by alkalis according to the equation:-

$$Li_2SiF_6 + 6NaOH \rightarrow 6NaF\downarrow + Si(OH)_4\downarrow + 2LiOH.$$

The solution is filtered and neutralized with hydrochloric acid.

A process is described for the recovery of lithium chloride in the preparation of lithium aluminium hydride.[206] The reaction of lithium hydride, aluminium chloride and ether gives a solution of lithium aluminium hydride and lithium chloride, which separates as an impure solid. The residue is heated in vacuum or an inert atmosphere between 30°C. and 650°C. The reactions, in order of occurrence with increasing temperature, are:-

(i) removal of ether;
(ii) $AlH_3.O(C_2H_5)_2 \rightarrow Al$, H_2 and $(C_2H_5)_2O$;
  $LiAlH_4 \rightarrow Al$, H_2 and LiH;
(iii) NH_4Cl reacts with Li and Al compounds to give LiCl, $AlCl_3$, H_2 and ammonia;
(iv) $AlCl_3$ volatilizes with some NH_4Cl and LiCl;
(v) $AlCl_3$ volatilizes, leaving LiCl.

PHYSICAL PROPERTIES

Structure.

Anhydrous lithium chloride has a cubic structure of the sodium chloride type. It has been shown that lithium chloride crystallizes in this form whether obtained from solution, the vapour phase or a fused system.[13]

The unit cell contains 4 molecules and at 25° C. has a = 5·1396 A.[14] Earlier work[15] gave the unit cell dimension at 25°C. as 5·12952 ± 0·00004 A.

Determinations of the lattice constant of lithium chloride by electron diffraction gave results agreeing to within 1·5% with those obtained by X-ray methods.[16] The growth of lithium chloride deposited from the vapour phase on cleavage surfaces of lithium fluoride, sodium chloride, potassium chloride and potassium bromide has been studied by electron diffraction. It was found in all cases that the crystallographic axes were parallel to those of the substrate.[17] Similar experiments involving deposition on muscovite showed a mismatch of 30% for lithium chloride.[18]

Early work by Hendricks[19] on the structure of lithium chloride monohydrate showed it to be tetragonal. This has more recently been confirmed[20] and the lattice constants calculated as a = 5·410 A., c = 3·81 A.

Molecular Volume.

The molecular volume of lithium chloride is 20·53.[21]

The absolute contraction constant, defined as the ratio of the molecular volume to the sum of the atomic volumes of the elements, is 0·69.[22]

The apparent molecular volume (Φ) of LiCl was determined at 18·1°C. and 0·5 M. LiCl concentration in water/organic-solvent mixtures (see Table I).[201]

TABLE I.- APPARENT MOLECULAR VOLUMES OF LITHIUM CHLORIDE AT 18·1°C. IN 0·5 M. SOLUTIONS

Water–Ethyl Alcohol (Wt.-% EtOH)	Φ, c.c.
0	18·24
38·99	18·06
63·02	17·51
79·31	14·35
85·64	12·64

Water–Urea (Wt.-% Urea)	Φ, c.c.
0	18·05
10·21	18·59
19·75	19·98
33·04	20·76

Water–Urethane (Wt.-% Urethane)	Φ, c.c.
0	18·06
1·78	18·02
8·92	17·99
22·25	18·26
39·00	18·61

Density.

Anhydrous lithium chloride:-

0°C. 2·07578 ± 0·00018 g./c.c.[23]
25°C. 2·074 g./c.c.[14]

Aqueous lithium chloride (selected values):-[24]

Molarity	ρ at 25°C.
0·0899	1·0022
0·2235	1·0057

continued on following page.

Molarity	ρ at 25°C.
0·7300	1·0175
1·798	1·0410
4·222	1·0888

Coefficient of Linear Expansion.

For anhydrous lithium chloride the value is 44·76 × 10^{-6}.[14,15]

Compressibility.

The compressibility of anhydrous lithium chloride has been determined at pressures up to 12,000 atm.;[25] the value at 30°C. is 3·41 × 10^{-12}, and an error of less than 1% is claimed.

The compressibility of aqueous lithium chloride solutions over the pressure range 0–1000 bars has been studied.[26] It was found that the compression was a linear function of the square root of the concentration only in extremely dilute solution.

At higher pressures (100–300 megabars) the results in Table II have been obtained.

TABLE II.- COMPRESSIBILITY OF AQUEOUS LITHIUM CHLORIDE SOLUTIONS

(β = compressibility per c.c. per megabar)

$10^6\beta$		Concentration of LiCl (wt.-%)	
40·44	25°C.	2·333	[27]
38·64		4·493	
35·85		8·084	
25·62	35°C.	27·450	[28]
21·86		37·003	
20·44		41·020	

Solubility in Water.

Solubility data for lithium chloride in water[29] are given in Table III.

TABLE III.- SOLUBILITY OF LITHIUM CHLORIDE IN WATER

t, °C.	G. LiCl/100 g. solution
1·05	40·90
10·05	42·71
15·70	44·06
18·25	44·86
24·15	45·47
40·05	47·09
50·20	48·23
64·95	50·26
80·85	52·94
89·55	54·82
95·15	55·83
100·2	56·3
120·2	56·9
140·3	57·6
155·6	58·3

Other values[30,31] are in close agreement.

The transition $LiCl,2H_2O \rightarrow LiCl,H_2O$ takes place at 19·1°C., and the transition $LiCl,H_2O \rightarrow LiCl$ at 93·55°C.[29,32]

The solubility of lithium chloride in water decreases with increasing pressure.[33]

Solubility in Liquid Ammonia, Methyl Alcohol, Acetone and Quinoline.

See Tables IV, V,[38] VI,[43] and VII,[47] respectively. More recent work[39] on methyl alcohol has confirmed that the solubility is independent of temperature, but gives the solubility at 25°C. as 41·0 g. of LiCl per 100 g. of MeOH.[40] Earlier work on acetone[44] gave consistently higher solubilities.

TABLE IV.- SOLUBILITY OF LITHIUM CHLORIDE IN LIQUID AMMONIA

Temp. °C.	G. LiCl/100 g. NH_3
-33·9	0·538 [34]
-20 ± 2	0·814)
0 ± 0·05	1·532)
5 ± 0·05	1·799)
10 ± 0·05	2·106) [35]
15 ± 0·05	2·498)
20 ± 0·1	2·807)
30 ± 0·1	3·630)

TABLE V.- SOLUBILITY OF LITHIUM CHLORIDE IN METHYL ALCOHOL

Temp. °C.	G. LiCl/100 g. CH_3OH
0	45·2
10	44·2
15	44·0
20	43·8
30	43·8
40	44·1
50	44·4
60	44·6

TABLE VI.- SOLUBILITY OF LITHIUM CHLORIDE IN ACETONE

Temp. °C.	G. LiCl/100 g. solution
0	10·1052
5	9·7864
10	9·5656
15	8·8238
20	8·1043
25	7·6655
30	7·2082
35	6·8013
40	6·3008
45	5·9264
50	5·6123

TABLE VII.- SOLUBILITY OF LITHIUM CHLORIDE IN QUINOLINE

Temp. °C.	G. LiCl/100 g. quinoline
0	0·1515
25	0·3538
40	0·6175
45	1·0328
50	1·1107
56·4	1·1734

continued on following page

TABLE VII (continued)

Temp. °C.	G. LiCl/100 g. quinoline
67	1·2353
75	0·8180
96	0·4588

Solubility in Diacetone Alcohol.[45]

$S = 0{\cdot}06683 - 0{\cdot}000395t + 0{\cdot}00001636t^2$, where S is the weight of anhydrous salt dissolved at t°C. in 1 g. of solvent.

Solubility in Other Solvents.

Some individual solubility values in miscellaneous solvents are collected in Table VIII.

In addition, lithium chloride is reported to be appreciably soluble in *iso*-amyl alcohol,[42] and very sparingly soluble in methyl *iso*butyl ketone.[45]

TABLE VIII.- SOLUBILITY OF LITHIUM CHLORIDE IN MISCELLANEOUS SOLVENTS

Solvent	Temp. °C.	Solubility	Reference
Liquid sulphur dioxide	25·00 ± 0·02	0·00062 g./100 g. solution	36
Phosphorus oxychloride	20	0·05 g./l.	37
Ethyl alcohol	25	24·7 g./100 g. EtOH	41
n-Propyl alcohol	25	16·0 g./100 g. PrOH	41
n-Butyl alcohol	25	12·2 g./100 g. BuOH	41
Acetonitrile	18	0·15 g./100 g. MeCN	40
Acetonitrile	25	0·14 g./100 g. MeCN	40
Formic acid	18	26·6 g./100 g. HCO_2H	40
Formic acid	25	27·5 g./100 g. HCO_2H	40
Tetrahydrofuran		Approx. 2 g./100 ml. solvent	46

Vapour Pressure.

A platinum-iridium crucible has been used to determine the vapour pressure of fused lithium chloride.[48]

Temp. °C.	Pressure, mm.Hg
1169	144
1247	276
1333	542
1384	770

More recent work[49,50] has been concerned with the rate of volatilization of lithium chloride in gas streams. Samples weighing 0·25 g. were maintained at 550°C. for 1 hr. in the stream.

Gas flow	% Loss in weight
Air	0·48
10 l./hr. HCl	0·08
6 l./hr. water vapour	0·90

At 800°C. the rate of evaporation of the chloride increases in the order Li, K, Rb, Cs and Na, and also with increase in the polarity of the gas used.

Vapour Pressures of Aqueous Solutions.

The vapour pressure of water above saturated solutions of lithium chloride has been determined (Table IX; the last value is from ref.[29], the remainder from ref.[51]).

The volatility of lithium chloride from an aqueous 0·1N. solution is reported to be nil.[52]

TABLE IX.- VAPOUR PRESSURES OF SATURATED LITHIUM CHLORIDE SOLUTIONS

Temp. °C.	Pressure, mm.Hg
23·90	2·63
29·90	2·93
34·90	5·32
39·90	7·26
44·90	9·82
54·84	16·70
80·15	37·9
100·30	78·3
119·85	173·9
140·05	334·4
160·30	615·4
180·20	1035·8

The water activity a_w for saturated lithium chloride at 25°C. is given by the expression:-[53]

$$a_w = p/p_0 = 0{\cdot}1105,$$

where p = vapour pressure of the solution and p_0 the vapour pressure of water at the same temperature.

The relation between temperature and the relative humidity over saturated lithium chloride solution has been determined[54] (Table X).

TABLE X.- RELATIVE HUMIDITIES OVER AQUEOUS SOLUTIONS SATURATED WITH LITHIUM CHLORIDE ($LiCl,H_2O$)

Temp. °C.	% Relative Humidity
0	14·7
10	13·3
20	12·4
30	11·8
40	11·6
50	11·4

Vapour Pressures of Lithium Chloride-Methylamine Complexes.[55] (Temperatures (T) are in °K.).

$LiCl,CH_3NH_2 \rightarrow LiCl + CH_3NH_2$, for the range 45–125°C.;
$\log p_{\text{mm.}} = 11{\cdot}5113 - 2656{\cdot}5/T$

$LiCl,2CH_3NH_2 \rightarrow LiCl,CH_3NH_2 + CH_3NH_2$, for the range 25–100°C.;
$\log p_{\text{mm.}} = 10{\cdot}8484 - 2604{\cdot}6/T$

$LiCl,3CH_3NH_2 \rightarrow LiCl,2CH_3NH_2 + CH_3NH_2$, for the range 10–95°C.;
$\log p_{\text{mm.}} = 9{\cdot}7460 - 2147{\cdot}5/T$.

Surface Tension of Aqueous Solutions and Fused Salt.

The surface tension of aqueous solutions of lithium chloride has been determined by the drop-weight method.[56]

Concentration (moles salt/l.)	σ (dynes/cm.)
1·08	74·74
1·94	76·22
3·51	79·46

The effect of hydrochloric acid on the surface tension of aqueous lithium chloride has been studied;[57] the acid reduces the surface tension, the effec increasing with increasing lithium chloride concentration.

The surface tension of fused lithium chloride at 750°C. is 127 dynes/cm.[58]

Viscosity of Aqueous Solutions.

Relative viscosities of aqueous lithium chloride and lithium chloride in dilute hydrochloric acid,[24] compared with pure water, have been determine (Table XI).

TABLE XI.- RELATIVE VISCOSITY OF LITHIUM CHLORIDE SOLUTIONS

Aqueous LiCl (25°C.)		Aqueous LiCl (25°C.) in 0·1018 M-HCl	
Wt. Molarity	Rel. Visc.	Wt. Molarity	Rel. Visc.
0·2235	1·0342	0	1·0070
0·7300	1·1075	0·2526	1·0415
1·798	1·2761	0·5001	1·0788
4·222	1·7391	1·0015	1·1556
		2·002	1·3168
		4·135	1·7282

The effect of temperature has also been studied (Table XII).[59]

TABLE XII.- EFFECT OF TEMPERATURE ON RELATIVE VISCOSITY OF LITHIUM CHLORIDE SOLUTIONS

Temperature	35·5°C.		45·3°C.		54·9°C.
Concentration (molal)	Rel. Visc.	Concentration (molal)	Rel. Visc.	Concentration (molal)	Rel. Visc.
0·319	1·0424	0·318	1·0416	0·318	1·0394
0·102	1·0118	0·102	1·0076	0·102	1·0045
0·032	1·0045	0·032	1·0028	0·032	1·0011
0·016	1·0020	0·019	1·0015	0·019	1·0006

It has been shown[60] that very thin films of aqueous lithium chloride behave as perfect fluids to within 0·1°C. of the f.p. The viscosity of the film is the same as that of the liquid in bulk. Gas viscometers of the Rankin type have been used for measuring the absolute viscosity of liquids;[61] for 12·03N. lithium chloride a value of 0·09017 ± 0·0007 has been obtained.

Diffusion in Aqueous Solutions.

Experimental methods for the determination of diffusion coefficients have been extensively studied by Harned.[62,63] It is now possible both by the conductance method, involving a measurement of change of concentration by means of a change of conductance in a diaphragm cell, and the Guoy layer interference method, involving the interference phenomena accompanying the deflection of light by gradients of refractive index, to study the Nernst theory as developed by Onsager and Fuoss.[64] Some data for lithium chloride are listed in Table XIII.

The effect of the presence of other ions including the lithium ion on the diffusion rate of the hydrogen ion has been investigated.[67] It has been shown that hydrogen ions may be almost stopped or accelerated as much as 40% above their normal velocity.

The diffusion of lithium chloride in sugar solution has been studied.[68] In the range 0·25–2·0M. sugar there is a steady decrease in the diffusion coefficient. In 2M. sugar solution the relative velocities of diffusion for alkali halides are in the order:-

$$LiCl > NaCl > KCl,$$

which is the reverse of the sequence for pure water.

TABLE XIII.- DIFFERENTIAL DIFFUSION COEFFICIENTS FOR AQUEOUS LiCl AT 25°C. (Selected values)

Concentration (moles LiCl/l.)	Diffusion Coefficient (cm.^{2}/sec. × 10^{-5})	Ref.
0 (Nernst limiting value)	1·368	
0·000634	1·348	65
0·00235	1·335	
0·00568	1·319	
0·0110	1·313	
0·05	1·280	66
0·10	1·269	
0·50	1·278	
1·0	1·302	
2·0	1·363	
3·0	1·430	

Thermodynamic Properties.

Heat of Formation.

For the reaction:-

$$Li + \tfrac{1}{2}Cl_2 \rightarrow LiCl,$$

ΔH°_{298} = -91,612 kg.-cal.[69] A more recent determination[70] by direct chlorination of lithium gives the value -94,800 ± 0·6 kg.-cal.

Heat of Solution and Heat of Dilution.

The heat of solution of lithium chloride in water has been determined at various concentrations.

Concentration of LiCl		Heat of Solution
0 (infinite dilution)	71	+8·570 kg.-cal. (20°C.)
0·0427 moles/l.		+8·476 kg.-cal. (20°C.)
0 (infinite dilution)	72	+8·765 kg.-cal. (25°C.)
0·08 moles/l.	73	+8·740 kg.-cal. (25°C.)
19·92 moles/l.	72	+0·600 kg.-cal. (25°C.)

The differential heat of solution diminishes with increasing salt concentration much more rapidly than with the other alkali metal chlorides.

A study has been made[74] of the integral heat of dilution of lithium chloride in water and in deuterium oxide. The values for water were slightly greater at all concentrations. Similar studies on the differential heat of dilution showed the results to be almost identical.

Heat of Solution in Methyl Alcohol.

Five determinations[71] between 0·0070 moles/l. and 0·0495 moles/l. gave a value at infinite dilution of +12·38 kg.-cal./mole, at 20°C.

Heat of Solution in Ethyl Alcohol.

Three determinations[71] between 0·0072 moles/l. and 0·0158 moles/l. gave a value at infinite dilution of +12·93 kg.-cal./mole, at 20°C.

Heat of Dissociation.

It has been shown[75] that the heat of dissociation of lithium chloride may be calculated from the frequency of the first absorption maximum in the ultra-violet of the solid and of solid chlorine.

Heat Capacity, Heat Content and Specific Heat.

The apparent molal heat capacity (ϕ_c) has been determined[76] for aqueous solutions at 25°C. (Table XIV).

TABLE XIV.- APPARENT MOLAL HEAT CAPACITY OF AQUEOUS LITHIUM CHLORIDE SOLUTION

Concentration (m) (moles/l.)	ϕ_c (Selected av. values) (in g.-cal.)	Specific Heat (g.-cal. per g.)
0·0400	−16·8	0·9976
0·0897	−15·3	0·9948
0·1600	−13·7	0·9911
0·2504	−13·1	0·9863
0·4904	−12·0	0·9739
1·0000	−10·3	0·9494
2·4614	−7·41	0·8890

A large quantity of experimental data has been summarized[77] and the following generalizations reached. ϕ_c Is a linear function of $m^{1/2}$ for aqueous solutions of univalent strong electrolytes from infinite dilution to approximately $m = 2{\cdot}5$. $\overline{Cp}_2$ (the partial molal heat capacity of the solute) is also a linear function of $m^{1/2}$. These relations are expressed by the following formulae:-

$$\phi_c = \phi_c^0 + Am^{1/2};$$

$$\overline{Cp}_2 = \overline{Cp}_2^0 + {}^3\!/_2 Am^{1/2};$$

$$\phi_c^0 = \overline{Cp}_2^0.$$

Over the range 18–25°C., A is constant at 6·1. At 25°C. $\phi_c^0 = -16{\cdot}2$, $d\phi_c^0/dT = {}^2\!/_7$ per degree C.

Heat content data for aqueous solutions of lithium chloride have been converted to 18°C. and tabulated.[78] The extrapolation to infinite dilution is made by employing the Debye-Hückel theory of strong electrolytes. Values of $\phi_h^{18} - \phi_h^0$ (the relative apparent heat content of the solute) and of $\overline{H}_2^{18} - \overline{H}_2^0$ (the relative partial molal heat content of the solute) are listed in Table XV.

TABLE XV.- RELATIVE APPARENT HEAT CONTENT AND RELATIVE PARTIAL MOLAL HEAT CONTENT OF LITHIUM CHLORIDE IN AQUEOUS SOLUTION

Moles LiCl per 1000 g. water	$\phi_h^{18} - \phi_h^0$ (g.-cal./mole solute)	$\overline{H}_2^{18} - \overline{H}_2^0$ (g.-cal./mole solute)
0	0	0
0·01	41	61
0·04	78	113
0·09	112	159
0·16	141	197
0·25	168	234
0·36	194	271
0·64	245	347
1·00	297	433
1·44	355	537
1·96	419	658

Energy of Hydration.

The sum of the standard free energies of hydration of pairs of ions[79] is

Σ (LiCl) = 191·8 kg.-cal./mole.

Work of Polarization.

The work of polarization w is the change in electrostatic energy resulting from the removal of a positive or negative charge from a lattice point in an ionic crystal.[80] With a rigid lattice of the rock-salt type it is assumed that the removal is effected so rapidly that there is no displacement of any ion as a whole.

Ionic polarizabilities:-

α_+ (10^{-24}cm.^{3}) w_+ 3·14 e.V.

α_- (10^{-24}cm.^{3}) w_- 1·89 e.V.

Activity Coefficient.

The activity coefficient of lithium chloride has been calculated from e.m.f., vapour pressure and freezing point data[81] (see Table XVI).

TABLE XVI.- ACTIVITY COEFFICIENT OF LITHIUM CHLORIDE IN AQUEOUS SOLUTIONS

Molality (Selected values)	γ (0° C.) Freezing point method	γ (20° C.) Vapour pressure method	γ (25° C.) (e.m.f. method)
0·001	0·96	–	0·965
0·005	0·93	–	0·927
0·01	0·91	–	0·901
0·05	0·85	–	0·819
0·10	0·81	0·791	0·779
0·20	0·78	0·756	0·750
0·30	0·77	0·739	0·739
0·50	–	0·731	0·736
1·00	–	0·754	0·753
3·00	–	–	1·165

Values at higher concentration[82] are as follows:-

Molarity	γ (25° C.) (Isopiestic method)
5	1·98
10	9·36
15	31·50
20	61·70

Isoactive Concentration.

This is defined as the concentration of a salt solution in which the water activity coefficient is equal to that in pure water.[91] For lithium chloride at 25°C. the value is 0·70 molal.

Accurate measurements have been made of the activity of lithium chloride in aqueous solutions containing both lithium and caesium chlorides;[83] the system showed marked deviations from simple behaviour.

Activity coefficients have been determined by radiochemical measurements on lithium chloride solutions containing potassium chloride and radioactive ^{24}Na, which were equilibrated with ion-exchange resins at 25°C.[84]

The change in activity coefficient of lithium chloride in water-methanol mixtures at various concentrations is similar in form to the corresponding change in aqueous lithium chloride[85] (Table XVII).

The graph of activity against square root of molal concentration drops in each case to a minimum at $\sqrt{m} = 0{\cdot}7$.

TABLE XVII.- ACTIVITY COEFFICIENT OF LITHIUM CHLORIDE IN METHANOL-WATER MIXTURES

(Activity coefficients are referred to the value 1·00 at infinite dilution in each solvent mixture.)

Solvent	γ in 0·5 molal LiCl	γ in molal LiCl
H_2O	0·73	0·77
10% MeOH 90% H_2O	0·68	0·73
20% MeOH 80% H_2O	0·64	0·68
30% MeOH 70% H_2O	0·60	0·64
40% MeOH 60% H_2O	0·56	0·60
50% MeOH 50% H_2O	0·52	0·56
60% MeOH 40% H_2O	0·46	0·49
70% MeOH 30% H_2O	0·40	0·43
80% MeOH 20% H_2O	0·34	0·37
90% MeOH 10% H_2O	0·26	0·29

The activity coefficient has been determined experimentally in water-ethyl acetate mixtures at 30°C.[199] (Table XVIII).

TABLE XVIII.- ACTIVITY COEFFICIENTS OF LITHIUM CHLORIDE IN WATER-ETHYL ACETATE MIXTURES

Concentration LiCl (Molar)	G. ethyl acetate per 100 g. water	γ (LiCl)
0·1	7·36	1·046
0·2	7·17	1·074
0·3	6·91	1·115
0·4	6·67	1·154

Activity in Ethyl Alcohol.

This has been determined by the boiling-point elevation method.[86] Data are given in Table XIX.

TABLE XIX.- ACTIVITY COEFFICIENT OF LITHIUM CHLORIDE IN ETHYL ALCOHOL SOLUTIONS

Molality	γ
0·01	0·1437
0·05	0·0631
0·10	0·0463
0·20	0·0330
0·40	0·0245
0·60	0·0212

Activity in *iso*Amyl Alcohol.

This has been found[92] from the distribution coefficient of lithium chloride between *iso*amyl alcohol and water in the range 8·6–0·15 M/1000 g. water solution. The values agree with those derived by the Debye–Hückel theory.

Activity in Formamide.

The melting points of formamide solutions of lithium chloride have been determined.[87] By assuming the cryoscopic constant for formamide to be 3·166 the following results were obtained.

Concentration (moles LiCl/kg. formamide)	γ
0·02	0·942

continued on following page.

Concentration (moles LiCl/kg. formamide)	γ
0·10	0·929
0·50	1·009
0·80	1·107

Activity in Acetonitrile.[88]

The activity coefficient of lithium chloride in acetonitrile has been determined from measurements of the e.m.f. of lithium-amalgam drop electrodes in double concentration cells using acetonitrile as electrolyte.

Miscellaneous Activity Data.

The phase diagram of the system LiCl–KF has been studied[89] and the activity of the components calculated (see Table XX).

TABLE XX.- ACTIVITY COEFFICIENTS OF LITHIUM CHLORIDE IN MIXTURES WITH POTASSIUM FLUORIDE

Temp. °C.	γ LiCl
879	1·00
870	1·02
843	1·05
815	1·04
783	0·99
759	0·97
723	0·92

The activity coefficient of LiCl in the melt system LiCl–AgCl has been determined at 600°C. from measurements on the cell:-[90]

$$Ag_{(s)} \mid AgCl \text{ in } LiCl_{(l)} \mid Cl_{2(g)}.$$

Data are given in Table XXI.

TABLE XXI.- ACTIVITIES OF LITHIUM AND SILVER CHLORIDES IN MOLTEN BINARY MIXTURES

Mole fraction AgCl	Activity AgCl	Activity LiCl
0	0·0	1·0
0·2	0·42	0·83
0·4	0·60	0·78
0·6	0·66	0·62
0·8	0·81	0·40
1·0	1·0	0

Transport Number, Dissociation and Solvation.

The transport numbers of the alkali chlorides at a given concentration are in the order Li < Na < K. This is unexpected in that the lightest ion, Li^+, would be expected to have the highest velocity; the anomaly is caused by the greater hydration of the Li^+ ion in solution.

Values of the transport number have been measured by the Hittorf method; selected values are given in Tables XXII and XXIII.

TABLE XXII.- TRANSPORT NUMBERS FOR Li^+ IN AQUEOUS LITHIUM CHLORIDE SOLUTIONS AT 25°C.[93]

Concentration (Normality)	T_+
0	0·3337 (at infinite dilution)
0·01	0·329

continued on following page

TABLE XXII (continued)

Concentration (Normality)	T_+
0·02	0·327
0·05	0·323
0·10	0·319

TABLE XXIII.- TRANSPORT NUMBERS FOR Li^+ IN WATER-METHANOL SOLUTIONS OF LITHIUM CHLORIDE AT 25°C.[101]

Mole fraction CH_3OH	Concentration LiCl (equivalent/l.)	T_+
0·0000	0·0500	0·3211
0·1006	0·05130	0·3242
0·2008	0·05146	0·3292
0·4027	0·05177	0·3412
0·6020	0·05019	0·3601
0·8024	0·05054	0·3804

In a given solvent the degree of solvation of lithium chloride decreases with increase in concentration. At a given concentration the solvation decreases with the complexity of the solvent molecule.[94] Hydration numbers have been calculated from determinations of the salting-out of oxygen from aqueous solution by the addition of lithium chloride:-[95]

LiCl (0°C.) 23
LiCl (20°C.) 21.

The hydration number of the lithium ion in lithium chloride solution, extrapolated to infinite dilution, is $X_{Li^+} = 26{\cdot}9$.[96] By a cryoscopic determination, the hydration of the ions in molar and 0·5 M. lithium chloride, respectively, at 15°C., correspond to $LiCl, 15H_2O$ and $LiCl, 17{\cdot}8H_2O$.[97] A method for establishing the degree of hydration of LiCl is described,[204] in which aqueous solutions of lithium chloride are extracted with 2-octanol. The results are represented diagrammatically in Fig. 1.

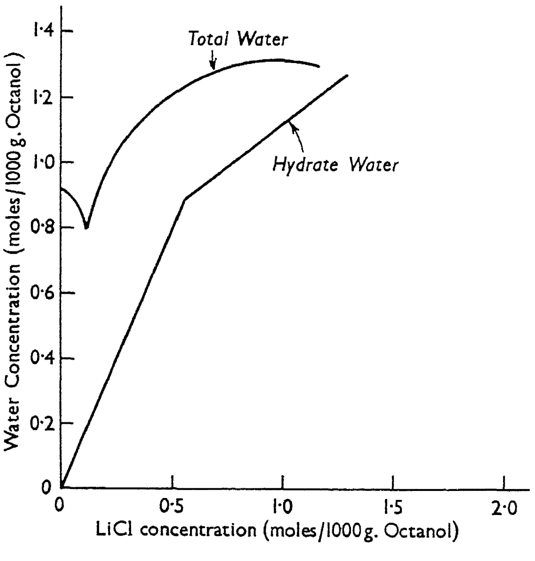

FIG. 1. HYDRATION OF LITHIUM CHLORIDE EXTRACTED FOR AQUEOUS SOLUTIONS BY OCTANOL

The solvation of lithium chloride in aqueous solutions of organic acids has been studied.[98] The degree of solvation increased with increasing numbers of carbon atoms, but decreased with increasing numbers of carboxyl groups. Solvation of lithium chloride in the system $H_2O–C_2H_5OH$ has been studied.[99] Ions remain solvated with water molecules until the proportion of ethyl alcohol exceeds 20 moles per cent.

Solvation of Lithium Chloride in Acetone.

Over the ranges 0·004–0·274 mole/l. at 18°C. and 0·008–0·271 mole/l. at 25°C., the solvation number was 5·14 to 5·57.[100]

Dissociation of Lithium Chloride.

Transference and conductivity measurements have been made for 0·05 N. solutions of sodium chloride and lithium chloride in water/methanol mixtures.[101] In a given solvent the Cl^- ion conductivities of the two salts are nearly identical, in accordance with the view that the solutes are completely dissociated. Lithium chloride has been shown to be a strong electrolyte in anhydrous acetic acid.[102]

The Raman spectra of salts in concentrated hydrochloric acid solutions have been studied.[103] No Raman scattering other than that of water is observed with aqueous lithium chloride solution up to 13 N. Aqueous hydrochloric acid (16·2 molal) containing the chloride (4 or 5 molal) gave a sharp Raman line at 2866 cm.$^{-1}$, indicating the presence of undissociated LiCl molecules.

Conductivity.

The specific conductance of fused lithium chloride has been determined by several workers.[104-107] Fairly close agreement is reported by the first three workers (Table XXIV).

TABLE XXIV.- SPECIFIC CONDUCTANCE OF FUSED LITHIUM CHLORIDE

Temp. °C.	*K*	Ref.
620	5·87	106
622·8	5·6923	105
631	5·94	106
681	6·14	106
700	6·14	104
702	6·21	106
712·5	6·2253	105
746	6·40	106
762	6·44	106
783·3	6·5309	105
786	6·53	106
801	6·59	106

In one case[105] a platinum–rhodium crucible was used, and attack is reported to have occurred above 783·3°C. When a platinum crucible was used[107] in an attempt to obtain results in the 780–930°C. range, much higher values of *K* were recorded.

The equivalent conductivity has also been determined (Table XXV).

TABLE XXV.- EQUIVALENT CONDUCTIVITY OF FUSED LITHIUM CHLORIDE

Temp. °C.	Λ	Ref.
650	160·65	109
700	173·03	109
707	181	110
750	182·81	109
800	193·6	109

The electrical conductivity of anhydrous lithium chloride has been studied between −180°C. and its melting point.[108] Ohm's Law is obeyed, and the dependence of conductivity on temperature is in agreement with Vant Hoff's equation. Conductance data for the system LiCl–KCl are given in Tables XXVI and XXVII.

TABLE XXVI.- SPECIFIC CONDUCTANCE OF THE SYSTEM LiCl–KCl[105]

Mole-%	Temp. °C.	*K*
100% LiCl	622·8	5·6923
	712·5	6·2253
	783·3	6·5399
81·77% LiCl 18·23% KCl	551·8	3·2440
	642·5	3·7124
58·80% LiCl 41·20% KCl	389·8	1·1819
	486·0	1·7964
	588·3	2·3375
40·45% LiCl 59·55% KCl	634·2	2·0726
	737·5	2·4734
19·96% LiCl 80·04% KCl	706·9	2·0765
	765·4	2·2644
	855·7	2·4975

TABLE XXVII.- MOLECULAR CONDUCTANCE OF THE SYSTEM LiCl–KCl[109]

Mole-% LiCl	Λ			
	650°C.	700°C.	750°C.	800°C.
0	–	–	97·80	106·23
10	–	–	99·08	106·20
20	–	91·69	100·00	110·20
30	89·71	97·55	105·95	115·71
40	92·20	102·35	111·97	120·72
50	94·82	104·29	114·51	124·05
60	113·01	121·67	129·75	–
70	117·81	127·21	135·54	143·21
80	122·57	131·24	140·59	150·08
90	138·57	147·72	158·99	167·83
100	160·55	173·03	182·81	193·16

The conductivity of aluminium bromide rises sharply when lithium chloride is dissolved in it;[111] on electrolysis of the solution aluminium separates at the cathode and bromine at the anode.

In the system $LiCl–CdCl_2$[112] the phase diagram indicates the formation of intermediate phases in the solid state, and the equivalent conductivity isotherm shows marked negative deviations from linearity; this is thought to indicate that the mixtures in the melt are more covalent than the pure compounds.

Conductivity in Aqueous Solutions.

Conductivity data for dilute aqueous lithium chloride solutions are listed in Table XXVIII. An equation representing Λ in terms of concentration (up to 0·1 N.) has been proposed by Fuoss and Onsager.[116] At higher concentrations and temperatures the values in Table XXIX have been obtained.[117]

A complete formula to cover the range up to saturation has been derived by Falkenhagen and Leist.[118]

TABLE XXVIII.- EQUIVALENT CONDUCTIVITY OF DILUTE AQUEOUS LITHIUM CHLORIDE SOLUTIONS

Concentration (equivalents/l. × 10^4)	Λ (25°C.)	Ref.
0	115·03*	
4·7210	113·18	
23·455	111·04	
58·840	108·91	
107·786	107·03	113
199·375	104·64	
499·42	100·10	
640·21	98·70	
1000	95·83	
5	113·13	
10	112·39	
20	111·33	114,115
30	110·56	
50	109·34	

* Limiting value

TABLE XXIX.- EQUIVALENT CONDUCTIVITY OF CONCENTRATED AQUEOUS LITHIUM CHLORIDE SOLUTIONS AT ELEVATED TEMPERATURES

Concentration (N.)	Λ 40°C.	60°C.	80°C.	100°C.
0·5	144·4	191·43	251·48	309·86
1	134·67	181·51	232·72	287·43
2	119·93	157·84	201·27	248·04
3	103·51	137·76	175·14	214·49
4	90·51	120·23	153·60	185·44
5	78·51	104·22	132·02	160·08
6	67·38	89·52	113·50	137·82
7	57·13	76·06	99·69	118·28

Conductivity of Aqueous Mixtures.

Conductivities have been determined for aqueous lithium chloride solutions containing hydrochloric acid,[24] methanol,[10] ethanol,[120] and pyridine;[121] for data, see Tables XXX to XXXIII, respectively.

Measurements of the conductivity of solutions of lithium chloride and sucrose at 20°C. showed that Walden's Law ($\lambda\eta$ = const.) was not obeyed, the value of this product increasing with increase in sucrose concentration.[119]

TABLE XXX.- SPECIFIC CONDUCTIVITY OF AQUEOUS LITHIUM CHLORIDE SOLUTIONS CONTAINING HYDROCHLORIC ACID[24]

(Weight molarity of HCl, 0·1010)

Concentration of LiCl (weight molarity)	Specific Cond. (κ) × 10^3
Nil	39·35
0·09955	46·24
0·2008	53·19
0·4055	66·30
0·817	90·10
2·104	143·65
3·834	183·76

TABLE XXXI.- EQUIVALENT CONDUCTIVITY OF SOLUTIONS OF LITHIUM CHLORIDE IN AQUEOUS METHANOL[101]
(at 25°C.)

Mol. fraction CH_3OH	Concentration of LiCl, equivalents/l.	Λ
0·0000	0·05000	100·14
0·1006	0·05130	67·85
0·2008	0·05146	54·03
0·4027	0·05177	46·24
0·6020	0·05019	46·52
0·8024	0·05054	49·75

TABLE XXXII.- EQUIVALENT CONDUCTIVITY OF SOLUTIONS OF LITHIUM CHLORIDE IN AQUEOUS ETHANOL[120]
(at 25°C.)

Concentration of LiCl (g.-equivalents/l.)	Λ	
0·08	40·30	30 wt.-% C_2H_5OH
0·01	45·94	
0·00125	48·06	
0·000625	48·83	
Limiting value	49·30	
0·08	33·43	40 wt.-% C_2H_5OH
0·01	38·52	
0·00125	40·27	
0·000625	40·93	
Limiting value	41·70	

TABLE XXXIII.- EQUIVALENT CONDUCTIVITY OF SOLUTIONS OF LITHIUM CHLORIDE IN AQUEOUS PYRIDINE[121]
(Pyridine concentration 18·86 mole-%)

Molar concentration LiCl	Λ
0·003972	44·02
0·001970	44·83
0·0009771	45·68
0·0004846	46·28
0·0002403	46·55

Conductivity in Organic and other Non-aqueous Solvents.

Methyl and Ethyl Alcohols.

Data are given in Tables XXXIV and XXXV.

Acetophenone.[124]

Determinations in the range 0·005–0·0005 M. only were possible owing to the extremely low solubility. A limiting value of $\Lambda_0 = 40$ was derived.

*cyclo*Hexanol.

Concentration of LiCl (N. x 104)	Λ (25°C.)
0·5424	0·599
1·1415	0·473 [125]
2·1505	0·350

continued on following page

Concentration of LiCl (N. × 104)	Λ (25°C.)
3·6370	0·321
5·2781	0·282 [125]
6·3505	0·266

A limiting value of 1·09 is given.

TABLE XXXIV.- EQUIVALENT CONDUCTIVITIES AT 25°C. OF SOLUTIONS OF LITHIUM CHLORIDE IN METHYL AND ETHYL ALCOHOLS

	Concentration of LiCl (equivalents/l. × 10^4)	Λ	
CH_3OH (Ref.[114])	1	89·74	(Limiting value given as 92·20)
	2	88·70	
	5	86·65	
	10	84·52	
	20	81·74	
	30	79·73	
	50	76·73	
C_2H_5OH (Ref.[123])	1·036	37·42	(Limiting value given as 39·20)
	2·054	36·76	
	4·412	35·62	
	8·950	34·10	
	13·964	32·88	
	19·654	31·76	

TABLE XXXV.- EQUIVALENT CONDUCTIVITIES OF SOLUTIONS OF LITHIUM CHLORIDE IN METHYL AND ETHYL ALCOHOLS, AT 0–40°C.[122]

	Concentration of LiCl:	0·25 N.	N.	1·5 N.	2 N.	3 N.
	Temp. °C.			Λ		
CH_3OH	0	27·2	13·2	-	6·9	3·8
	10	31·4	15·7	-	8·1	4·8
	20	36·0	18·3	-	9·8	5·9
	30	41·0	21·1	-	11·7	7·2
	40	46·2	24·2	-	13·7	8·6
	(A limiting value of 90·9 is given.)					
C_2H_5OH	0	7·2	3·1	2·0	-	-
	10	8·9	3·95	2·55	-	-
	20	10·3	4·85	3·25	-	-
	30	12·1	6·0	4·1	-	-
	40	14·1	7·25	5·1	-	-
	(A limiting value of 90·9 is given.)					

Further work has been done more recently[126] which indicates that the Debye-Hückel limiting law holds for solvents of low dielectric constant (including *cyclo*hexanol) if the Bjerrum ion association is taken into account.

Nitromethane containing Aluminium Bromide.

Aluminium bromide dissolves readily in nitromethane to give a colourless solution in which lithium chloride is readily soluble. The presence of the chloride raises the specific conductivity of the mixture considerably, and during electrolysis lithium separates at the cathode.[127]

Ethyl Bromide containing Aluminium Bromide.

A similar system $LiCl-AlBr_3-C_2H_5Br$, has been studied[128] and has similar properties. For the system $AlBr_3-C_2H_5I$[203] addition of lithium chloride decreases the conductivity if the $AlBr_3 : C_2H_5I$ ratio is 0·24. At ratios above 0·44 the conductivity is raised by lithium chloride. Electrolysis of the mixture gives aluminium crystals.

N-Methylacetamide.[205]

Determinations were carried out between 30 and 60°C., in which range the dielectric constant of the solvent varied between 178·9 and 138·6. Results over the concentration range 5×10^{-4} M.–2 M. indicated the complete dissociation of lithium chloride; some data are given below.

Temp. °C.	Λ_0	$\Lambda_0\eta$
30	14·1	0·550
40	18·1	0·548
50	22·4	0·543
60	27·4	0·536

Hydrogen Cyanide.

Anhydrous hydrogen cyanide is a powerful dissociating medium for lithium chloride. The conductivity of solutions has been studied in the range 0·002 N. to 0·0001 N. at 18°C. A limiting value (Λ_0) of 345·5 has been derived.

Phosphorus Oxychloride.

The solubility of lithium chloride in anhydrous phosphorus oxychloride is 0·05 g./l. at 20°C. At this concentration the specific conductivity (κ) is $6{\cdot}6 \times 10^{-6}$ ohms^{-1}cm.$^{-1}$.[37]

Decomposition Potential.

The decomposition potential of fused lithium chloride at 800°C.[130] is 3·17 V. (extrapolated to zero current). Earlier workers[131] obtained rather higher figures. For the system $LiCl-AlBr_3$ the decomposition potential is 1·60 V.[111]

The fused system LiI–LiCl has also been investigated;[134] the iodine overvoltage is independent of lithium iodide concentration between 25 and 100% LiI.

Decomposition Potential in Methyl Alcohol.[132]

A sharp break in the current-voltage curve at 1·20 V. indicated the decomposition potential. A second break at 1·90 V. was thought to be due to traces of water. The e.m.f. of the cell:-

$$Li \mid 0{\cdot}01\ N.\ LiCl\ in\ CH_3CN \mid 0{\cdot}01\ N.\ AgNO_3\ in\ CH_3CN \mid Ag$$

is 2·476 V. at 25°C.[133]

Dielectric Constant.

The value for anhydrous lithium chloride (10·62 at 18°C., measured at 1800 m. wave-length) has been obtained by immersing the salt in a liquid between the plates of a condenser; the nature of the liquid was varied until the total capacity was not changed by the presence of the salt.[135]

In aqueous solution the value has been obtained by the Fürth ellipsoid method.[136] The graph of dielectric constant against lithium chloride concentration falls from infinite dilution to a minimum value of 73·5 at 7 N., recrosses the value for water at 15 N. and then continues to rise steadily. An explanation of the variations has been attempted[137] in terms of ordering of the solvent molecules around the solvated ions.

Magnetic Susceptibility.

Values for anhydrous lithium chloride at 20° C.:-

$$-\chi_m \times 10^{-6} = 24{\cdot}2^{138}$$

$$-\chi_m \times 10^{-6} = 24{\cdot}6.^{139}$$

In aqueous solution at 20° C.:-

$$-\chi_m \times 10^{-6} = 24{\cdot}2^{140}$$

$$-\chi_m \times 10^{-6} = 24{\cdot}3.^{138}$$

The same value has been obtained for solutions in 94·2% C_2H_5OH.

The variation of specific susceptibility with concentration has been been determined at 29° C.[141]

LiCl (%)	$-\chi_m \times 10^{-6}$ (selected values)
4·12	0·716
9·66	0·712
16·28	0·707
22·59	0·696
32·80	0·679
44·49	0·665

The complete plot of the figures shows that two lines may be drawn, giving molecular susceptibility constants over two concentration ranges:-

0–19% LiCl, -27×10^{-6}

28–44% LiCl, $-25{\cdot}4 \times 10^{-6}$.

Miscellaneous Physical Properties.

(i) Refractive Index of anhydrous lithium chloride, 1·663.[14]

(ii) Molecular Refraction.

The molecular refraction of aqueous lithium chloride solutions was determined in the concentration range 2·77–43·87% LiCl and between 6° and 70°C. Extrapolation of the graph gave a figure of 7·76 for the D line (25° C.) for 100% LiCl.[142]

(iii) Infra-red Absorption.[143]

By use of a quartz cell and monochromatic radiation the following results were obtained with aqueous 6 N. lithium chloride:-

	Wave-length (μ)					
	52	63	83	100	117	152
Reflecting power (% R)	11·20	12·73	13·28	13·39	13·40	14·40
Absorption Coeff. (na)	0·43	0·48	0·41	0·35	0·32	0·35
Index of Refraction (n)	1·87	1·96	2·04	2·08	2·09	2·15

(iv) Dipole Moment.

For the isotopic pair ^{6}LiCl and ^{7}LiCl the difference in dipole moment is 1·8 millidebyes.[144]

(v) Soret Coefficient.

The coefficients of 0·05 N. lithium chloride at various temperatures are as follows:-[145]

Temp. °C.	30	40	50	60
Soret Coefficient	0·31	0·28	0·96	1·27

(vi) Coefficient of Internal Friction.

The following values are given:-[146]

650°C. $\eta \times 10^2 = 3{\cdot}02$

850°C. $\eta \times 10^2 = 2{\cdot}10$.

SYSTEMS CONTAINING LITHIUM CHLORIDE (WITHOUT WATER OR ORGANIC COMPOUNDS)

Three-Component Systems.

(i) Li, Be || Cl[147]

In the cooling curve there is a maximum at 360°C. indicating the compound Li_2BeCl_4. A eutectic melting at 300°C. contains 0·56 mole $BeCl_2$ and 0·44 mole LiCl.

(ii) Li, Hg || Cl[148]

The maximum solubility of LiCl in $HgCl_2$ is 1·9 mole-%. A eutectic mixture melting at 278°C. contains 1·6 mole-% LiCl. The boiling temperature of the mixture is 297°C.

(iii) Li || Cl, BO_2[149]

LiCl is completely dissociated in $LiBO_2$.

Four-Component Systems.

(i) Li, Ag || Cl, SO_4[150]

The stable diagonal AgCl-Li_2SO_4 is a binary characterized by the practically complete insolubility of the components indicated by a straight line at 818°C. from 2–98·8% Li_2SO_4. The unstable diagonal LiCl–Ag_2SO_4 consists of six crystallization branches. In the triangle AgCl, Li_2SO_4, Ag_2SO_4 there is a triple eutectic, m.p. 290°C. The thermal effect of the system is high (17·80 kg.-cal./equiv.) with a pronounced shift of equilibrium to the stable pair Li_2SO_4 and AgCl.

(ii) Li, Ag || Cl, NO_3[151]

The diagonal AgCl–$LiNO_3$ is a stable system of almost complete miscibility. The diagonal $AgNO_3$–LiCl was studied up to 82 mole-% LiCl (m.p. 484°C.); above this concentration LiCl decomposed the melt. Conjugate liquid phases appear between 26% and 77% LiCl at 325°C. and 456°C. The diagonal AgCl–$LiNO_3$ divides the system into two ternaries, $LiNO_3$–AgCl–LiCl (having a triple eutectic at 250°C. containing 0·5% AgCl and 87·5% $LiNO_3$) and $LiNO_3$–AgCl–$AgNO_3$.

(iii) Li, Ca || Cl, SO_4[152,153]

The eutectics of the binaries in this system are:-

LiCl–Li_2SO_4	480°C.	(52·5 mole-% Li_2SO_4)
LiCl–$CaCl_2$	475°C.	(53 mole-% $CaCl_2$)
LiCl–$CaSO_4$	533°C.	(25 mole-% $CaSO_4$)

$CaCl_2$-Li_2SO_4 627°C. (13·5 mole-% Li_2SO_4)
600°C. (87·5 mole-% Li_2SO_4)

LiCl-$CaCl_2$ mixtures form no compounds.

(iv) Li, Cd || Cl, SO_4[154]

The system reacts irreversibly in the direction: $2LiCl + CdSO_4 \rightarrow CdCl_2 + Li_2SO_4$; ΔH = 7·99 kg.-cal./equiv. Li_2SO_4-$CdSO_4$, $CdCl_2$-$CdSO_4$ and LiCl-Li_2SO_4 are all eutectic systems, whereas the system LiCl-$CdCl_2$ exhibits continuous solid solution with a minimum.[155] Earlier work[156] indicated the presence of compounds $3CdCl_2,4LiCl$ and $3CdCl_2,2LiCl$, but this has not been substantiated. Data for the minima are:-

LiCl-Li_2SO_4	53 mole-% Li_2SO_4	478°C.
LiCl-$CdCl_2$	77-78 mole-% $CdCl_2$	500°C.

The only stable cross-section is the diagonal joining the reaction products $CdCl_2$ and Li_2SO_4. This binary system has a monotectic three-phase region from 8-80% Li_2SO_4 at 650°C. and a eutectic at 3·5% Li_2SO_4 at 543°C. Other cross-sections are metastable with immiscible liquids forming from primary solid. The equivalent conductivity isotherm of the system LiCl-$CdCl_2$ shows marked negative deviation from linearity.[112]

(v) Li, Co || Cl, SO_4[157]

The system $2LiCl + CoSO_4 \rightleftharpoons Li_2SO_4 + CoCl_2$ has been studied by the visual polythermal method. The system LiCl-$CoCl_2$ showed a continuous series of solid solutions with a minimum at 517°C. containing 50 mole-% $CoCl_2$. The phase diagram showed a stable binary system $CoCl_2$-Li_2SO_4 with a eutectic at 548°C. containing 65 mole-% Li_2SO_4. The cross-section of the unstable LiCl-$CoSO_4$ system showed four branches, $\alpha + \beta$ LiCl, β $CoCl_2$ and $CoSO_4$.

(vi) Li, Cs || Cl, SO_4[158]

The two diagonals of the system CsCl-Li_2SO_4 and LiCl-Cs_2SO_4, are unstable. The diagonal CsCl-Li_2SO_4 intersects the crystallization fields CsCl, Li_2SO_4,Cs_2SO_4, $4Li_2SO_4,Cs_2SO_4$ and Li_2SO_4. The other diagonal intersects the fields of the two compounds and $LiCl,Cs_2SO_4$ and Li_2SO_4. The system LiCl-CsCl has a eutectic at 332°C. with 58 mole-% LiCl and a transition at 397°C. corresponding to the polymorphous transition of CsCl. Invariant ternary points:-

	Mole-%				
Temp. °C.	LiCl	CsCl	Li_2SO_4	Cs_2SO_4	Phases
Eutectic 530°	-	68	10	22	CsCl, Cs_2SO_4, Li_2SO_4,Cs_2SO_4
Eutectic 326°	53	43·5	3·5	-	LiCl, CsCl, Li_2SO_4
Transition 458°	18	52	30	-	CsCl, Li_2SO_4, Cs_2SO_4, $4Li_2SO_4,Cs_2SO_4$
Transition 450°	24·5	41·5	34	-	CsCl, Li_2SO_4, $4Li_2SO_4,Cs_2SO_4$.

(vii) Li, K || Cl, SO_4[159, 160]

This is an irreversible reciprocal system with the equilibrium shifted in favour of the stable pair Li_2SO_4-KCl (6·4 kg.-cal./equiv.) The system LiCl-KCl has a eutectic at 354°C. at 41·7 mole-% KCl.[161]

(viii) Li, K || Cl, OH[162]

The equilibrium KOH + LiCl ⇌ LiOH + KCl is shifted strongly towards LiOH-KCl (20·54 kg.-cal./equiv.) which is the stable diagonal. In the system LiOH-LiCl, the compound LiOH,LiCl is formed, which forms a eutectic melting at 262°C. with LiOH, containing 37 mole-% LiCl.

(ix) Li, K || Cl, NO_3[163]

(x) Li, NH_4 || Cl, NO_3[164]

Two ternary eutectics are given:-

$NH_4NO_3, LiNO_3, NH_4Cl$	84°C.
$LiNO_3, LiCl, NH_4Cl$	95°C.

(xi) Li, Na || Cl, SO_4[165]

The system is an irreversible reciprocal one with the stable diagonal $NaCl-Li_2SO_4$ having a eutectic at 499°C. containing 74 mole-% Li_2SO_4. The binary system LiCl-NaCl formed the incongruently melting compound LiCl, NaCl and had a eutectic at 553°C. containing 78·5 mole-% LiCl. LiCl undergoes a α-β homeomorphic transition at 565° C. and 81·5 mole-% LiCl.

(xii) Li, Pb || Cl, VO_4[166]

Eutectics:-

392°C.	79% $PbCl_2$,	13% LiCl,	8% Li_3VO_4
464°C.	64% $PbCl_2$,	21% LiCl,	15% Li_3VO_4.

(xiii) Li, Rb || Cl, F[167]

The binary systems LiF–RbF and RbF–RbCl and the main systems were studied by visual polythermal methods. The surface of the liquidus of the systems consisted of four fields of pure components.

(xiv) Li, Sr || Cl, F[168]

The system $LiCl-SrCl_2$ was studied. Neither compounds nor solid solutions are formed. The eutectic point is at 487°C. and 54 mole-% $SrCl_2$. The main system is a simple example of a completely irreversible system of the non-diagonal type.

(xv) Li, Zn || Cl, SO_4[169]

The reaction is irreversible in the direction $2LiCl + ZnSO_4 \rightarrow Li_2SO_4 + ZnCl_2$. The binary compound $ZnCl_2,2LiCl$ (incongruent m.p. 352°C.) was found.

Invariant points (all composition expressed in mole-%):-

Eutectic	285°C.	13 LiCl	0·5 Li_2SO_4	86·5 $ZnCl_2$
Eutectic	293°C.	9 $ZnSO_4$	0·7 Li_2SO_4	90·3 $ZnCl_2$
Transition	330°C.	35·5 LiCl	2·0 Li_2SO_4	62·5 $ZnCl_2$
Transition	397°C.	28·7 $ZnSO_4$	5·0 Li_2SO_4	66·3 $ZnCl_2$.

(xvi) Li, K, Na || Cl[170]

LiCl–KCl forms no compounds; the eutectic point is at 361°C. and 58 mole-% KCl. LiCl–NaCl forms a continuous series of mixed crystals, the eutectic being 552°C. and 72 mole-% LiCl.

The main system has a eutectic at LiCl 51·5 mole-%, NaCl 11·5 mole-% and KCl 37 mole-%.

(xvii) Li, K, Rb || Cl[171]

RbCl and LiCl form a double salt LiCl,RbCl of incongruent m.p.

Five-Component Systems

(i) Li, K || Cl, SO_4, WO_4[172,173,174]

Extensive information on the phase relations in this very complex system is given.[172-174]

(ii) Li, K, Na || Cl, SO_4[175]

The cross-sections Li_2SO_4-Na_2SO_4-KCl and Li_2SO_4-Na_2SO_4-NaCl are both unstable. The presence of NaCl in the fusion of sulphates favours the appearance of $2Li_2SO_4,K_2SO_4$, but is less favourable to the transformation of Li_2SO_4,K_2SO_4; KCl favourably influences the appearance of Li_2SO_4,Na_2SO_4 and $Li_2SO_4,2Na_2SO_4$.

The quaternary transformation point is shown at 436° C. and 24% NaCl, 51% Li_2SO_4, 25% K_2SO_4.

AQUEOUS SYSTEMS CONTAINING LITHIUM CHLORIDE

(i) H_2O-LiCl-$BaCl_2$

This system is reported as forming no compounds,[176,177] but later workers[178] suggest the possibility of complex formation.

(ii) H_2O-LiCl-$BeCl_2$

The solubility isotherms have been studied at 0° C.[179] and 25° and 40° C.[176] No double salts are formed. At a composition of 17·2% LiCl and 25·8% $BeCl_2$ the solid phase is LiCl,H_2O and LiCl,$2H_2O$. At a composition 13·3% LiCl and 29·4% $BeCl_2$ the solid phase is LiCl,H_2O and $BeCl_2,4H_2O$.

(iii) H_2O-LiCl-$CaCl_2$[176,177]

No double salts are formed.

The solution has two univariant equilibria $CaCl_2,2H_2O$ and $CaCl_2,4H_2O$ at a composition of 8·25% LiCl and 39·78% $CaCl_2$, and $CaCl_2,2H_2O$ and LiCl,H_2O at 24·06% LiCl and 22·11% $CaCl_2$.

(iv) H_2O-LiCl-$CdCl_2$[176]

The system formed the compound LiCl,$CdCl_2$,$2{\cdot}5H_2O$.

(v) H_2O-LiCl-$CoCl_2$

This system has been studied through its solubility isotherm[180] and by interfacial tension against *iso*amyl acetate.[181] The double salts $CoCl_2$, 4LiCl,$10H_2O$ and $CoCl_2$,2LiCl,$4H_2O$ were found.

(vi) H_2O-LiCl-$CuCl_2$

In this system the following solid phases separate: LiCl,H_2O, LiCl,$2H_2O$, LiCl,H_2O + LiCl,$CuCl_2$,$2H_2O$, LiCl,$CuCl_2 2H_2O$, LiCl,$CuCl_2$,$2H_2O$ + $CuCl_2,2H_2O$ and $CuCl_2,2H_2O$.[182,183] LiCl,$CuCl_2$,$2H_2O$ forms deep red hygroscopic needles. Study of the system at low temperature[184] has resulted in the discovery of 4LiCl,$CuCl_2$,$10H_2O$. The isotherm at 0° C. shows that this salt can exist in equilibrium with LiCl,$CuCl_2$,$2H_2O$ and LiCl,$2H_2O$. The salt decomposes to LiCl,$CuCl_2$,$2H_2O$ in water. Study of the system by the interfacial tension method has indicated the formation of four complexes;[185] the interfacial tension against *n*-butyl acetate is plotted against additions of $CuCl_2$ to LiCl.

Addition of 0·025M. $CuCl_2$ to 0·025M. LiCl indicates that the complexes

$3LiCl,CuCl_2$, $2LiCl,CuCl_2$, $LiCl,CuCl_2$, $LiCl,2CuCl_2$ are formed.

Addition of 0·5 M. $CuCl_2$ to 0·5 M. LiCl similarly indicate the existence of $LiCl,CuCl_2$, and $LiCl,2CuCl_2$.

(vii) H_2O-LiCl-CsCl[186]

The isotherms of this system at 25°C. and 40°C. show the formation of $2CsCl,LiCl,4H_2O$.

(viii) H_2O-LiCl-$HgCl_2$[176,187]

The isotherm at 30°C. was studied. No compounds were formed. The solubility of $HgCl_2$ was increased by the presence of LiCl.

(ix) H_2O-LiCl-$MgCl_2$[188]

Isotherms at 102°, 70°, 30° and 25°C. were studied and the existence of $LiCl,MgCl_2,7H_2O$ was established.

(x) H_2O-LiCl-$MnCl_2$[189]

In addition to LiCl, $LiCl,2H_2O$, $MnCl_2,2H_2O$ and $MnCl_2,4H_2O$, the stability of the following double salts was established:-

$4LiCl,MnCl_2,10H_2O$	0–28°C.
$2LiCl,MnCl_2, 4H_2O$	23–76°C.
$LiCl,MnCl_2, 2H_2O$	Above 53°C.
$2LiCl,MnCl_2, 2H_2O$	Above 73°C.
$LiCl,MnCl_2, 5H_2O$	From below 0°C. to 26°C.

(xi) H_2O-LiCl-NH_4Cl[190]

No compounds are reported.

(xii) H_2O-LiCl-$NiCl_2$[182]

The polytherms of the system between 0° and 100°C. showed the following solid phases: $NiCl_2,2H_2O$, $NiCl_2,4H_2O$, $NiCl_2,6H_2O$, $NiCl_2,LiCl,2H_2O$, $NiCl_2,2LiCl,4H_2O$ and $NiCl_2,4LiCl,10H_2O$.

(xiii) H_2O-LiCl-$PbCl_2$

No double salts were found at 25°C.[191] or at 50°C.[192] Solubility data for the two salts are as follows:-

Concentration (g./1000 g. of water)

LiCl	$PbCl_2$		
-	10·87		
	↓	falling to	
43·77	1·39		Solid phase $PbCl_2$
	↓	rising to	
735·2	103·5		
	↓	falling slightly	
834·9	101·6	(eutectic)	Solid phase $PbCl_2$ + $LiCl,H_2O$

The $PbCl_2$ solubility then drops to zero with the second phase $LiCl,H_2O$ separating.

Isodynes of $PbCl_2$ in solutions of alkali metal chlorides were prepared. For alkali metal chlorides of the same ionic strength, the activity coefficient of $PbCl_2$ is greatest in the presence of LiCl and least in the presence of KCl.

(xiv) H_2O-LiCl-RbCl[186]

The isotherms at 25°C. and 40°C. show the presence of 2LiCl,RbCl,$4H_2O$ and LiCl,3RbCl,$2H_2O$.

(xv) H_2O-LiCl-$SrCl_2$[176,177]

No compounds are reported.

(xvi) H_2O-LiCl-$ZnCl_2$[176,183]

The following compounds are reported:-

2LiCl,$ZnCl_2$,2·5H_2O;

2LiCl,$ZnCl_2$,5H_2O.

(xvii) H_2O-LiCl-Li_2SO_4[194]

The solubility isotherm was studied at 25° C. The curve is composed of two branches, corresponding with the crystallization of Li_2SO_4,H_2O and LiCl,H_2O. There is a sharp decrease in the solubility of Li_2SO_4, which can be quantitatively precipitated by LiCl.

(xviii) H_2O-LiCl-NaCl-KCl[195]

The isotherms were studied at 0–25° and 50°C. No compounds were formed. The solubilities of NaCl and KCl are markedly decreased by the presence of LiCl in the solution.

SYSTEMS CONTAINING LITHIUM CHLORIDE AND ORGANIC COMPONENTS

(i) H_2O-LiCl-C_2H_5OH[196,197]

Investigation of the system down to −55°C. indicated the presence of LiCl,3C_2H_5OH and LiCl,5C_2H_5OH. LiCl crystallized at the following temperatures and compositions:-

3·53 mole-% LiCl,H_2O	−9·1° C.
6·95 mole-% LiCl,H_2O	−23·5° C.
8·06 mole-% LiCl,H_2O	−30·4° C.
10·2 mole-% LiCl,H_2O	−47·2° C.

At 25°C., LiCl and LiCl,H_2O separate, but there is no evidence of alcoholate formation.

(ii) H_2O-LiCl-C_3H_7OH[198]

The liquidus contour of the system shows a pronounced lowering of temperature of initial crystallization of the solution with the addition of C_3H_7OH. At all concentrations of LiCl under 5·6 mole-% the system is a homogeneous liquid; at higher concentrations, two phases form.

(iii) H_2O-LiCl-$CH_3COOC_2H_5$[199]

LiCl (molar concentration)	G. $CH_3COOC_2H_5$/100 g. water 25° C.	30° C.	35° C.	40° C.
0·1	7·64	7·36	7·08	6·81
0·2	7·48	7·17	6·85	6·54
0·3	7·23	6·91	6·58	6·25
0·4	6·99	6·67	6·34	6·02

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(iv) $H_2O-LiCl-(C_2H_4)_2O_2$[200]

Saturated aqueous LiCl was prepared at room temperature, and excess dioxan was added; LiCl separated as:-

$LiCl,H_2O,(C_2H_4)_2O_2$.

(v) CH_3OH-LiCl-Benzoic acid[202]
C_2H_5OH-LiCl-Benzoic acid
$(CH_3)_2CO$-LiCl-Benzoic acid
$(CH_3)_2CO$-LiCl-Salicylic acid
$(CH_3)_2CO$-LiCl-Tartaric acid.

A salting out by LiCl was observed with methyl and ethyl alcohols. The solubility of the acid in acetone was increased by LiCl.

CHEMICAL PROPERTIES

In general the chemical properties of lithium chloride are straightforward and well known. Some more recently investigated aspects are outlined here.

The hydrolysis of lithium chloride has been studied between 550° and 900°C.[207] The reaction is favoured by high temperature, and good yields of hydrogen chloride are not obtained until above the melting point. The addition of silica or meta-kaolin greatly improves the yield as it reacts with the free Li_2O.

At higher temperatures (1100°C. approx.) there is evidence that hydrogen and lithium chlorides react with silica to give Li_2SiCl_6.[208]

Lithium chloride reacts readily with boric acid at 300°C. to give lithium metaborate.[209]

The reaction between lithium chloride and sodium cyanide has been studied at 570°C.[210] In the presence of iron powder as a catalyst 8·4% of Li_2CN_2 (lithium cyanimide) was formed after 30 hr.

A study of the corrosion resistance of various metals and alloys to fused lithium chloride has shown it to be most corrosive.[211] Good resistance to corrosion, even in the presence of air, is obtained with alloys of the "Hastelloy" type.

The absorbability of a number of metal ions, (e.g., $Mn^{\cdot\cdot}$, $Sc^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Co^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ga^{\cdot\cdot\cdot}$ and $Au^{\cdot\cdot\cdot}$) from lithium chloride solution on anion-exchange resins has been studied.[212] Although the activity coefficients of lithium chloride and hydrochloric acid are similar, the adsorption from lithium chloride of the same concentration was very much greater.

Lithium chloride is readily absorbed on anion-exchange resins from acetone solution,[213] probably in the form of $(LiCl_2)^+$ complexes.

The exchange between lithium chloride and synthetic cation-exchange resins has also been studied.[214] The order of cations in acetone was found to be the same as in water. The percentage of cation taken by the resin was found to increase linearly with increasing acetone concentration in aqueous mixtures.

Lithium chloride is frequently used in organic reactions as a catalyst. In the catalytic cleavage of ethyl chloride into ethylene and hydrochloric acid, it is quite effective.[215] The oxidation of carbon, in the free state or combined, by potassium chlorate has been extensively studied.[216] Carbon black, (343°C.) bakelite (367°C.), and a mixture of styrene copolymers and 4:4′-di*iso*propenyldiphenyl (390°C.) all react much more vigorously with potassium chlorate in the presence of lithium chloride.

In the preparation of acetal from the reaction of acetaldehyde and ethyl alcohol, excellent results are obtained using lithium chloride as catalyst.[217]

The halolysis of the ester $(C_2H_5)_3PO_4$ by lithium chloride has been studied.[218] In water or acetic acid an ethyl group is excluded as ethyl chloride leaving $(C_2H_5)_2HPO_4$. At 200° C. the ester and lithium chloride react readily to give $(C_2H_5)_2LiPO_4$. In general[219] lithium chloride does not react with esters of phosphorous acid of the type $(RO)_3P$ at room temperature, but does so vigorously on heating to give $(RO)_2PLi$.

Lithium chloride is usually the preferred reagent for the monodebenzylation of neutral benzyl esters of the oxyacids of phosphorus,[220] e.g.:-

$$(\mathrm{Ph\ CH_2O})_2\ \mathrm{PO(OPh)} \xrightarrow[\substack{\mathrm{LiCl} \\ 89\%}]{\substack{100^\circ\mathrm{C.} \\ 3\ \mathrm{hr.}}} (\mathrm{PhCH_2O})\ \mathrm{PO.OH\ (OPh)}.$$

APPLICATIONS

Lithium chloride mixed with potassium chloride to form a eutectic mixture is the starting material for the preparation of lithium by electrolysis. On a small scale lithium has been made satisfactorily from lithium chloride by reduction with barium.[221] The reactants are heated at 850° C. in a bomb under argon; 99·5% pure lithium can be obtained by reheating the first product with lithium chloride.

Lithium chloride is frequently used to lower the operating temperature of fused electrolytic baths.

In the electrolytic preparation of titanium[222,223] $TiCl_3$ may be added to the eutectic mixture, 60 mole-% LiCl and 40 mole-% KCl. The mixture melts at 343° C. and is electrolyzed under argon or hydrogen between tungsten electrodes.

Systems of the type $KCl-LiCl-AlCl_3$ and $KCl-LiCl-MgCl_2-AlCl_3$[224] are used in the electrolytic production of aluminium. Such systems melt in the range 670–730° C. and are used for the production of the liquid metal over a wide range of concentration.

Molybdenum powder is produced in the electrolysis of K_3MoCl_6 (25 wt.-%), LiCl (34%), and KCl (41%) at 600° C.[225]

Manganese and silver are obtained by electrolysis of the following salt mixtures:-

$$AgCl-LiCl-NaCl-KCl;$$
$$MnCl_2-LiCl-NaCl-KCl.$$[226]

A patent brazing flux[227] for titanium and zirconium and alloys containing these metals is made from the components of the system $LiF-KCl-KHF_2$. A patent melting flux[228] consists of 68% LiBr, 22% LiCl and 10% LiF, and is used for melting Mg-Li alloys, e.g., 68% Mg, 11% Li, 16% Cd, 5% Ag. A patent process is described[241] for coating steel or other ferrous materials with aluminium. A salt bath of the type KCl 38%, NaCl 28%, Na_3AlF_6 10%, AlF_3 5%, LiCl 19%, m.p. 1075°, is maintained as a layer above the molten aluminium. The article to be coated is held in the salt layer and then immersed in the molten aluminium. Lithium chloride may be used in the electrolyte of dry cells required for operation at very low temperatures.[229] An electrolyte consisting of $ZnCl_2$ 12%, LiCl 15% and NH_4Cl 8% gave 20% of the normal capacity at −40° F.

Lithium chloride is widely used in air conditioning plants.[230-236] It is considered superior to calcium chloride as it is one of the most hygroscopic of all inorganic compounds and can be used to dehumidify to 11% relative humidity at room temperature. It is non-toxic and has a high drying rate. A concentrated solution will not become entirely solid until below −60° F. The usual procedure is to recirculate foul air through a tower against a spray of lithium chloride solution, fresh air being bled in if necessary. Dust particles are readily coagulated and odours absorbed. The main lithium chloride feed is cooled and recirculated; approximately 10% is evaporated to drive off absorbed water.

In general it is thought to be cheaper to attain low humidities by the use of chemical drying agents rather than by refrigeration.[237] The limitations on drying pressures are practically eliminated by removing water vapour with a liquid absorbent. A ·1 mm. pressure can be readily maintained by lithium chloride solution.[238]

A solution consisting essentially of lithium chloride and water has been used to prevent frost formation.[242]

Titanium dioxide (anatase) can be converted to rutile by heating between 400° and 1000°C., the needed temperature depending upon the origin of the anatase. The addition of small quantities of lithium chloride lowers the transition temperature.[239]

In mullitization the most powerful mineralizing agent is lithium present as the fluoride. Lithium chloride is also very effective, 1 mole-% giving a 100% conversion at 1400°C.[240]

The exothermic heat of reaction in catalytic cracking, hydrocarbon synthesis, polymerization, etc., may be removed by decomposable hydrated salts, e.g., $LiCl,H_2O$. At the temperature of reaction the hydrate is decomposed to the chloride and steam absorbing large quantities of heat and hence acting as a moderator to the reaction. $LiCl,H_2O$ may be used between 200 and 1100°C. and may be regenerated with steam between 70 and 160°C.[243]

In the preparation of ethylene oxide from ethylene, using silver promoted with beryllium oxide as a catalyst, small additions of lithium chloride to the catalyst improve the conversion efficiency.[244]

Synthetic resin sheets may be prepared by polymerizing a layer of liquid resin on a salt solution to give a casting.[245] The optical qualities of the castings prepared using lithium chloride were very good; they were clear and free from bubbles.

A mixture of potassium chloride and lithium chloride may be used for removing fission products from uranium-bismuth fuels.[262] Rare-earth metals dissolved in liquid bismuth can be extracted nearly quantitatively in this way, while uranium remains in the metal phase.

A patent preparation[246] is described for inhibiting the build up of electrostatic charges on polythene films, fibres and coatings; it consists of an aqueous dispersion of 2% polyvinyl acetate, 0·5% lithium chloride and polymerized wood resin.

SPECTRA

In the infra-red region the addition of lithium chloride to water to give a 10 N. solution causes no change in the maximum at 1·47 μ. The entire band at 1·98 u, however, is shifted to a longer wave-length;[247] the shift is thought to be due to ion hydration.

The absorption of lithium chloride solution in the ultra-violet has been studied.[248] Values for the optical density of 3 N. solution 1 cm. thick are:-

	20°C.	40°C.	60°C.	80°C.
λ 2200 A.	0·027	0·035	0·056	0·094
λ 2300 A.	0·018	0·021	0·025	0·032
λ 2500 A.	0·01	0·012	0·014	0·016

A 0·5 N. solution of lithium chloride containing ammonium chloride and ammonia shows absorption in the ultra-violet.[249]

No Raman scattering other than that of water was observed with aqueous lithium chloride up to 13 N.[103] Aqueous hydrochloric acid (16·2 molal) containing lithium chloride (4–5 molal) gave a sharp Raman line at 2866 $cm.^{-1}$, indicating the presence of undissociated molecules. Some confirmation of these findings has been found using 60% lithium chloride solution.[250] A very faint band at approximately 4160 A. was found and also a possible new band at 4850 A.

The abnormal behaviour of lithium chloride in solution is again explained by its association with many water molecules.[251]

RADIATION CHEMISTRY

Measurements have been made of the angular correlation between annihilation quanta produced by positrons annihilating in lithium chloride.[252,253] Annihilation appears to occur only in the outer electrons of the negatively charged halogen ions.

Positive ion emission from lithium chloride has been studied.[254] The kinetic energy of the ions has been determined.

The scattering of copper K_α X-radiation has been determined in solutions of lithium chloride up to 13·3 moles per litre.[255] At high concentration the scattering of water is repressed. The data are incompatible with the assumption that there is a random distribution of ions in the solution, but indicates ions in a distorted water lattice. At high concentrations the whole structure is thought to become similar to a solid salt containing water.

Negative ions from a discharge in lithium chloride vapour may be drawn off and accelerated by a potential difference. A beam, thought to be $LiCl_2^-$, impinges on a metal target; this results in the liberation of positive ions.[256]

A target of lithium chloride bombarded with deuterons of energies up to 900,000 e.V. has given yields several hundred times as great as by bombarding beryllium with helium. At the maximum deuteron current of 30 microamps about 100 recoil particles per minute were obtained. This is about 100 times the intensity obtained by means of the strongest polonium α-particle sources.[257]

ANALYTICAL ASPECTS OF LITHIUM CHLORIDE CHEMISTRY

The effect of neutral salts on the indicator acidity function H_0 has been measured by spectrophotometric means in 0·01, 0·1 and 1 M. hydrochloric acid solutions, with the simple basic indicators 2:4-dichloroaniline, *p*-nitroaniline, diphenylamine and *o*-nitroaniline. In 0·01 and 0·1 M. acid the salt concentration effect is linear up to salt concentrations of 4 M., and is specific for the salt. The apparent acidity is increased by salts in the order:-

$$\text{LiCl} > \text{NaCl} > \text{KCl}.$$

The apparent acidity is decreased by tetramethylammonium and tetraethylammonium bromides.[258]

Lithium chloride has been potentiometrically and visually titrated in glacial acetic acid solution against 0·1 N. mercuric, lead and thallous acetates. The indicators used were potassium nitroprusside or dithizone for mercury, neutral red or thionine for thallium and neutral red, thionine or safranine for lead.[259]

A calomel electrode involving a half-cell of mercury, a mercury-mercurous chloride paste and ethylenediamine saturated with mercurous chloride and lithium chloride, is used in titrations of weak acids and bases in water-free solvents.[260]

The polarographic reductions of lead in methyl or ethyl alcohol and cadmium in methyl alcohol, ethyl alcohol or acetic acid were studied with lithium chloride as supporting electrolyte.[261] Acetyl chloride, propionyl chloride, butyryl chloride, *iso*valeryl chloride, benzoyl chloride, β-phenylpropionyl chloride, acetyl bromide, propionyl bromide and benzoyl bromide gave well-defined waves in acetone saturated with lithium chloride at 30°C.

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A calomel electrode made with lithium chloride instead of potassium chloride and acetone instead of water was found to be satisfactory.

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SECTION XII

LITHIUM BROMIDE

By W. P. DOYLE

Preparation

A suggested method of manufacture consists in treating di-lithium sodium orthophosphate, Li_2NaPO_4, with aluminium bromide or ferric bromide to precipitate the phosphate of aluminium or iron and form lithium bromide.[1] The manufacture of lithium bromide has been described in detail.[2]

Physical Properties

X-Ray diffraction studies of aqueous lithium bromide solutions show a broad ring, the position of which is independent of concentration; the ring is ascribed mainly to interference between the scattering from the bromide ion and that of the surrounding water molecules.[3]

An investigation of the anode-ray emission of lithium bromide confirmed the lithium line at 2934·1 A. previously observed and established a general correspondence with the helium spectrum.[4] The frequency of the lattice oscillations of lithium bromide has been calculated, on the basis of the Born model, to be $6{\cdot}7 \times 10^{12}$; the anharmonicity was also calculated.[5] Oriented overgrowths of lithium bromide on a potassium chloride substrate have been considered in their relation to lattice stability.[6] The electrical conductivity of solid silver bromide with added lithium bromide has been measured[7] from 200°–400° C.; the results are shown in Fig. 1, where the ordinate gives the conductivity relative to that of pure silver bromide at the same temperature and where, to avoid confusion, for each 25° C. difference in temperature the curves are displaced 0·1 of an ordinate unit relative to one another; the results show that the added lithium bromide forms a normal substitution lattice.[7] Values calculated theoretically for the lattice constant, energy content, compressibility and infra-red frequency of lithium bromide agree fairly well with observed values.[8] From a consideration of the relations between the lattice energies, melting points and boiling points of the alkali halides, it is suggested that lithium halides are more covalent than the other alkali halides.[9] The formation of lithium bromide is accompanied by the emission of ultraviolet radiation.[10] The dielectric constant of lithium bromide is 10·95.[11]

The molecular magnetic susceptibility of lithium bromide in aqueous solution is[12] $-36{\cdot}0 \times 10^{-6}$; this value has been confirmed.[13] The molecular magnetic susceptibility of solid lithium bromide is[13] $-34{\cdot}7 \times 10^{-6}$.

The magneto-optical rotation for Na D lines of aqueous solutions of lithium bromide has been measured.[14] The development of turbidity on cooling or heating mixed crystals of lithium and sodium bromides has been investigated and the results are given in Table I.[15]

The cubic compressibility of solid lithium bromide is reported as[16] $5{\cdot}0 \times 10^{-6}$ per megabar and as $4{\cdot}31 \times 10^{-12}$ reciprocal dynes per sq. cm. at 30° C.;[17] from the latter value the cubic compressibility at absolute zero is, by extrapolation, $3{\cdot}2 \times 10^{-12}$ reciprocal dynes per sq. cm.;[17] the change of compressibility with pressure is $24{\cdot}5 \times 10^{-12}$ reciprocal dynes per sq. cm. and is

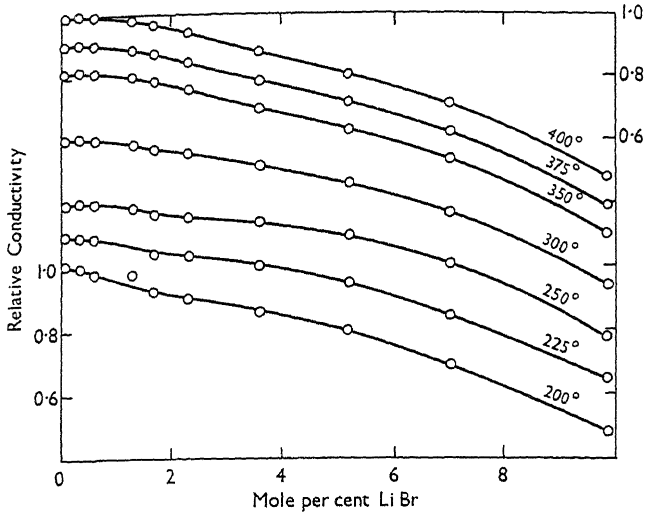

FIG. 1. CONDUCTIVITY OF LiBr–AgBr MIXED CRYSTALS

independent of temperature between 30° and 75°C.; the average change of compressibility with temperature is $8{\cdot}4 \times 10^{-4}$ reciprocal degrees centigrade between 30° and 75°C.[17] These experimental results have been discussed in relation to lattice theory.[16,17]

TABLE I.- TURBIDITY OF LITHIUM BROMIDE-SODIUM BROMIDE CRYSTALS

Mole fraction of NaBr	On cooling, development of turbidity		On heating, disappearance of turbidity	
	begins at (°C.)	ends at (°C.)	begins at (°C.)	ends at (°C.)
0·32	195	145	175	240
0·40	210	155	202	265
0·48	190	130	185	240
0·53	100	–	–	150

The densities[18] of molten solutions containing 0·5 mole fraction of lithium bromide in silver bromide are given in Table II; the values can be expressed by the relation $d^t = 4{\cdot}504 - 0{\cdot}000877t$.

TABLE II.- DENSITY OF LITHIUM BROMIDE-SILVER BROMIDE MELT
(mole fraction of LiBr = 0·5)

t°C.	517·4	527·6	533·4	545·6	550·0	555·2
Density, g./c.c.	4·051	4·041	4·036	4·026	4·022	4·017

The vapour pressures[19] of molten lithium bromide between 1114° and 1317°C. are given in Table III.

TABLE III.- VAPOUR PRESSURE OF MOLTEN LITHIUM BROMIDE

t°C.	1114	1117	1180	1204	1264	1309	1317
V.p. (mm.)	148·4	159·8	269·3	537·6	542·7	770·1	772·1

The refractive indices of molten silver bromide–lithium bromide solutions were measured as a function of temperature and concentration; the molar refractivity of the solutions was found to be an additive function of the mole fraction.[20]

The heat of sublimation of lithium bromide was calculated[21] to be between 15 and 35 kg.-cal. per mole using a previously developed equation[22] relating thermochemical properties to lattice structure. The heat of dissociation of lithium bromide vapour, determined by an optical method,[23] is 96·7 ± 1·4 g.-cal.[24] as compared with the thermochemical value 87·06 g.-cal. It is suggested that the optical method is not completely valid.[24]

The changes in free energy of molten silver bromide on dilution with lithium bromide have been determined;[18] the results, which are given in Table IV, have been discussed on the basis of simple assumptions as to ionization.

TABLE IV.- CHANGE IN FREE ENERGY (in g.-cal.) OF SILVER BROMIDE ON DILUTION WITH LITHIUM BROMIDE

t° C.	Mole fraction of AgBr				
	1·0000	0·5937	0·4086	0·2548	0·1100
500	0	-510	-780	-1000	-1890
550	0	-560	-880	-1150	-2140
600	0	-600	-960	-1270	-2390

The specific heats[25] from 10°–130° C. of aqueous solutions of lithium bromide of various concentrations are given in Table V; other determinations of the specific heat of aqueous solutions of lithium bromide have been reported.[26]

TABLE V.- SPECIFIC HEAT OF AQUEOUS SOLUTIONS OF LITHIUM BROMIDE

t° C.	Molality of solution		
	0·560	0·910	1·32
10	0·9456	0·9148	0·8822
20	0·9446	0·9143	0·8818
40	0·9470	0·9160	0·8842
60	0·9491	0·9201	0·8882
80	0·9520	0·9225	0·8901
100	0·9565	-	0·8935
120	0·9602	-	0·8955
130	0·9619	-	0·8967

In aqueous solution, the heats of solution and dilution of lithium bromide from extreme dilution up to saturation were determined at 25° C.;[27] the integral heat of dilution, the heat effect caused by the dilution of a solution containing 1 mole of salt from a particular initial concentration to infinite dilution, was determined and the results discussed in relation to the nature of solutions of strong electrolytes.[28,29] The concentration dependence of the heat of dilution for aqueous lithium bromide solutions agrees with that calculated on the basis of a modified Debye-Hückel theory.[30] The molar heat of solution of lithium bromide in liquid ammonia is[31] 19·715 kg.-cal. The apparent molal heat capacity, and hence the partial molal heat capacity, of lithium bromide in aqueous solution have been related to the concentration of the solution;[30-32] this correlation has been discussed in relation to the hydration of ions.[25] The concentration dependence of the apparent molar heat capacity of aqueous lithium bromide solution agrees with that calculated by means of a modification of the Debye-Hückel theory.[30]

The sum of the standard free energies of hydration of lithium and bromide ions was, from standard electrode potential and other data, calculated as 184·9 kg.-cal. per mole.[33] The total heat of hydration of lithium bromide has, from measurements of heat of solution and the value of the lattice energy, been critically selected as 194 kg.-cal. per mole; this value was used to obtain the heat of hydration of the simple lithium ion, Li^+, 121 kg.-cal. per g.-ion, and of the simple bromide ion, Br^-, 72 kg.-cal. per g.-ion; the results are discussed in relation to the nature of the hydration sphere.[34] The limit of full solvation was measured and discussed in relation to the structure of concentrated solutions of lithium bromide.[35] Information about the ions in a concentrated solution of lithium bromide has been derived from vapour pressure data.[36]

Three hydrates of lithium bromide have been observed[37] – the monohydrate, dihydrate and trihydrate. In a later investigation, a pentahydrate, stable below -49° C., was found.[38]

The solubilities of lithium bromide in methanol, acetonitrile and formic acid have been determined[39] at 18° and 25°C.; the results are given in Table VI.

TABLE VI.- SOLUBILITY (*S*) OF LITHIUM BROMIDE IN METHANOL, ACETONITRILE AND FORMIC ACID

Solvent	*t*°C.	*S*(g./100 g. of solvent)
Methanol	18	117
	25	140
Acetonitrile	18	8·2
	25	8·8
Formic acid	18	82
	25	80

The solubilities of lithium bromide in diacetone alcohol and in mesityl oxide have been determined[40] from 20° to 65°C.; the results are given in Table VII, where the solubility is the weight of anhydrous salt dissolved in one gram of solvent in the presence of the solid phase indicated.

TABLE VII.- SOLUBILITY OF LITHIUM BROMIDE IN DIACETONE ALCOHOL AND MESITYL OXIDE

t°C.	Solubility in diacetone alcohol, solid phase: $LiBr,2(CH_3)_2,C(OH).CH_2COCH_3$	Solubility in mesityl oxide, solid phase: $LiBr,(CH_3)_2C{=}CHCOCH_3$
20·0	0·1126	0·3401
35·0	0·1452	0·3677
50·0	0·2039	0·4063
65·0	0·2916	0·4550

A number of phase equilibrium studies of systems containing lithium bromide have been made. The following double compounds have been detected: (*a*) $LiBr,2LiOH$ in the system $LiBr$–$LiOH$–KBr–$LiOH$;[41] (*b*) $CoBr_2,LiBr$, and possibly $CoBr_2,2LiBr$, in the system $CoBr_2$–$LiBr$–H_2O–2-butanone;[42] (*c*) $LiBr,4CH_3OH$ in the system $LiBr$–CH_3OH;[43] (*d*) $LiBr,4C_2H_5OH$ in the system $LiBr$–C_2H_5OH;[44] (*e*) $LiBr,4n\text{-}C_3H_7OH$ in the system $LiBr$–$n\text{-}C_3H_7OH$;[43] (*f*) $LiBr,2(CH_3)_2CO$ in the system $LiBr$–$(CH_3)_2CO$.[45] In the system $AgBr$–$LiBr$ solid solutions are formed.[46] Analysis of the anhydrous system $LiBr$–$MgBr_2$ shows the presence of two series of mixed crystals, one being richer in magnesium bromide, the other in lithium bromide.[47] The system $MgBr_2$–$LiBr$–H_2O forms no compounds and the phase diagram shows a rather short $MgBr_2,6H_2O$

branch followed by a branch of solid solutions;[48] a later investigation of the same system confirmed that no double salts are formed but di-, tri- and penta-hydrates of lithium bromide and hexa- and deca-hydrates of magnesium bromide were found.[38] In the system $CaBr_2$–LiBr–H_2O there is a series of solid solutions, and in the $BaBr_2$–LiBr–H_2O system lithium bromide acts as a salting-out agent towards barium bromide.[49] In the system LiBr–H_2O–C_2H_5OH no alcoholates were detected and the solid phases recognized were anhydrous lithium bromide and the mono- and di-hydrate of lithium bromide.[50] Other systems that have been investigated are LiBr–RbBr[51] and $HgBr_2$–LiBr–H_2O.[52] A study of the precipitation of silver bromide in the presence of lithium bromide showed that in normal analytical practice there is no contamination of the precipitate by the formation of a solid solution.[53]

The densities at 35°C. of concentrated aqueous solutions of lithium bromide have been determined[54] and are given in Table VIII.

TABLE VIII.- DENSITY OF AQUEOUS LITHIUM BROMIDE SOLUTIONS

Wt.-% of LiBr	18•076	34•706	39•999	45•183
Density at 35°C., g./c.c.	1•13859	1•31036	1•37671	1•44911

The density of an aqueous solution containing 39•4% of lithium bromide has been measured[55] from −70° to 20°C. and the results are given in Fig. 2.

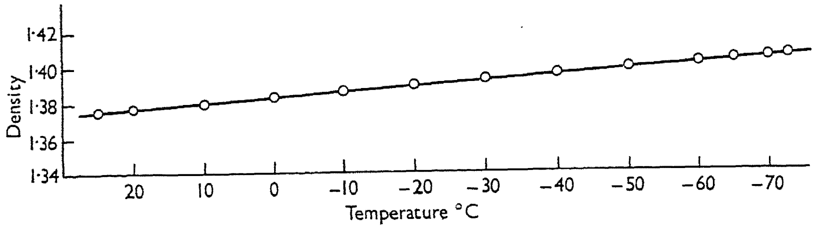

FIG. 2. DENSITY OF AQUEOUS SOLUTION CONTAINING 39•4% OF LITHIUM BROMIDE

For aqueous solutions of lithium bromide the thermal expansion between 20° and 40°C. and the specific volume at 25°C. have been determined;[56] representative thermal expansion data are given in Table IX, where $\Delta_t v$ is the change in specific volume resulting from a temperature change from 25•00°C. to the temperature indicated; specific volumes are given in Table X. From the data, the apparent volume expansion and expansibility were computed; there was no evidence of breaks in the curves of the apparent expansion plotted against the concentration between 20° and 35°C.[56]

For methanol solutions and for glycol solutions of lithium bromide, the thermal expansion and the specific volume at 25°C. have been determined.[57] $\Delta_t v$, the finite change in specific volume for a given rise of temperature, was expressed as a quadratic function of the temperature by the equation:-

$$\Delta_t v = A + B\,(t - 25) + C\,(t - 25)^2.$$

The coefficients of tne equation for methanol solutions of lithium bromide are given in Table XI and those for glycol solutions are given in Table XII.

Table XIII gives the specific volumes at 25°C. for methanol solutions and for glycol solutions of lithium bromide. The apparent molal expansibility is negative and increases with concentration; comparison of the data with those for aqueous solutions indicate that structural changes in water largely determine the expansion of aqueous solutions.[57]

TABLE IX.- THERMAL EXPANSION OF AQUEOUS LITHIUM BROMIDE SOLUTIONS

t°C.	20·00	22·50	25·00	27·50	30·00	32·50	35·00	37·50	40·00
Wt. fraction of LiBr in soln.	$\Delta_t v \times 10^5$								
0·04989	-121·1	-62·9	0·0	68·2	141·4	219·2	301·2	387·9	477·8
0·36962	-123·8	-62·5	0·0	62·8	127·5	192·6	258·2	325·1	392·4
0·54980	-116·4	-58·2	0·0	58·8	117·3	176·5	235·1	293·9	352·6

TABLE X.- SPECIFIC VOLUME (v) OF AQUEOUS LITHIUM BROMIDE SOLUTIONS AT 25°C. (x = weight fraction of LiBr in solution)

100x	v (ml.)	100x	v (ml.)
0·000	1·00293	25·221	0·82590
4·989	0·96724	36·962	0·74494
10·518	0·92816	39·375	0·72822
10·633	0·92735	39·918	0·72443
14·758	0·89850	44·980	0·68910
15·007	0·89678	54·980	0·61797
19·947	0·86240	60·551	0·57782

TABLE XI.- THERMAL EXPANSION OF SOLUTIONS OF LITHIUM BROMIDE IN METHANOL

Wt. fraction of LiBr in soln.	$A \times 10^5$	$B \times 10^5$	$C \times 10^5$
0·0000	0·0	152·5	0·338
0·07187	1·0	126·4	0·181
0·15833	0·9	100·9	0·115
0·24352	0·1	80·4	0·037
0·35114	0·1	59·7	0·035

TABLE XII.- THERMAL EXPANSION OF SOLUTIONS OF LITHIUM BROMIDE IN GLYCOL

Wt. fraction of LiBr in soln.	$A \times 10^5$	$B \times 10^5$	$C \times 10^5$
0·04069	0·0	53·1	0·070
0·08115	-0·1	50·0	0·036
0·12360	-0·1	46·9	0·034
0·20593	-0·4	41·0	0·003

The diffusion coefficients of aqueous solutions of lithium bromide have been measured;[58] the results are given in Table XIV where D_F is the diffusion coefficient calculated from Fick's equation and D_B that calculated from the Boltzmann equation.

Excellent agreement was obtained between the experimental results and those calculated on the basis of the Nernst–Planck theory of diffusion in electrolytes modified by using, as an approximation, Bjerrum's concept of association; this agreement permits the calculation of association as a function of concentration.[58]

The relative viscosity of an aqueous solution containing 39·4% of lithium bromide has been measured[55] from -70° to 20°C. and the results are shown in Fig. 3.

TABLE XIII.- SPECIFIC VOLUME (v) OF SOLUTIONS OF LITHIUM BROMIDE IN METHANOL AND IN GLYCOL AT 25°C.

(x = weight fraction of LiBr in solution)

Methanol solutions		Glycol solutions	
100x	v (ml.)	100x	v (ml.)
0·000	1·27136	1·9962	0·88827
4·033	1·22336	4·069	0·87524
7·187	1·18679	8·115	0·85019
11·711	1·13567	12·360	0·82430
13·264	1·11835	20·593	0·77509
15·833	1·08980	30·100	0·71947
24·352	0·99772	-	-
30·123	0·93742	-	-
35·114	0·88586	-	-

TABLE XIV.- DIFFUSION COEFFICIENTS FOR AQUEOUS SOLUTIONS OF LITHIUM BROMIDE

Ratio of initial concentrations					
10 : 0			5 : 0		
concentration (volume-%)	$D_F \times 10^6$	$D_B \times 10^6$	concentration (volume-%)	$D_F \times 10^6$	$D_B \times 10^6$
0·05	10·2	10·4	0·05	10·4	10·5
0·1	10·4	9·7	0·1	11·4	10·4
0·2	10·6	10·6	0·2	11·5	11·3
0·5	10·3	10·8	0·5	10·8	10·4
1·0	10·1	10·5	1·0	11·2	9·8
1·5	10·0	10·4			
2·0	9·8	10·5			

Ratio of initial concentrations		
10 : 2		
concentration (volume-%)	$D_F \times 10^6$	$D_B \times 10^6$
2·05	10·8	10·0
2·1	11·1	10·45
2·2	11·0	11·3
2·5	10·6	10·9
3·0	10·3	11·8
3·5	8·65	12·0
4·0	7·0	11·2

The theory of the viscosity of electrolyte solutions has been extended by introducing the concept of closest approach, but comparison of the values calculated for lithium bromide and other uni-univalent electrolytes with the experimental values shows that this treatment gives no improvement on the older theory.[59] The compressibility coefficients of concentrated aqueous solutions of lithium bromide have been measured[54] and are given in Table XV; on the basis of the measurements the irregular properties of concentrated solutions of lithium bromide have been discussed.

The concentration dependence of the compressibility of aqueous solutions of lithium bromide, calculated using a modified Debye-Hückel theory, agrees with experimental data.[30] The compressions, to 1000 bars, of solutions of

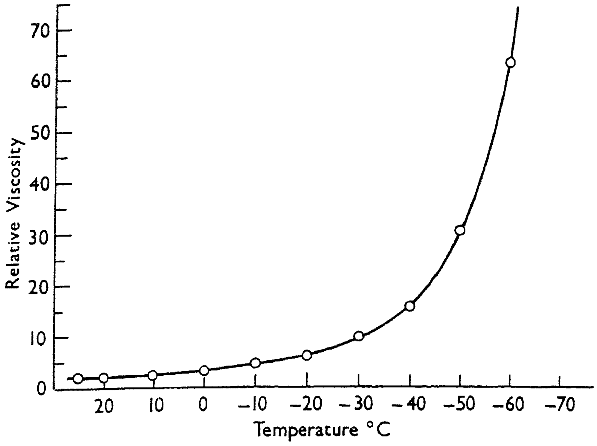

FIG. 3. RELATIVE VISCOSITY OF AQUEOUS SOLUTION CONTAINING 39·4% OF LITHIUM BROMIDE

lithium bromide in methanol and in glycol were measured and apparent volumes, compressions and effective pressures were calculated.[60]

TABLE XV.- COMPRESSIBILITY COEFFICIENT (β) OF AQUEOUS LITHIUM BROMIDE SOLUTIONS

Wt.-% of LiBr	18·076	34·706	39·999	45·183
$\beta \times 10^6$	35·28	30·11	28·63	27·12

The vapour pressure of aqueous solutions, containing from 50 to 68% of lithium bromide, has been expressed mathematically as a function of the absolute temperature.[61] Cryoscopic measurements of very dilute solutions of lithium bromide in *cyclo*hexanol gave results in complete agreement with those derived from the osmotic theory of Debye and Hückel.[62] Cryoscopic investigation of the complex $LiBr,2AlBr_3$ in benzene showed that the complex is very much associated and that the degree of association increases, with concentration; addition of lithium bromide to a benzene solution of aluminium bromide raises the freezing point, thus indicating a further association of aluminium bromide during the formation of complex compounds.[63] The molalities of isopiestic solutions at 25°C. for $LiBr–CaCl_2$ and $LiBr–H_2SO_4$ have been reported and used to calculate the osmotic coefficient for lithium bromide.[64] The freezing points of aqueous solutions of lithium bromide were measured.[65]

The decomposition potential of fused lithium bromide is 2·95V. and this experimental value agrees with those calculated by two different methods.[66] The decomposition potentials of a mixture of lithium bromide and aluminium bromide (equimolar amounts) in toluene is 3·5V., in xylene 3·4V., in ethyl bromide 3·6V., in ethylene dibromide 3·6V., in nitromethane 3·8–4·0V. and in nitrobenzene 5·1V.; for a mixture containing 2 moles of aluminium bromide for each mole of lithium bromide the decomposition potentials are 2·3V. in benzene, 2·6V. in toluene, 2·9V. in xylene, 2·0V. in ethyl bromide, 2·0V. in ethylene dibromide, 2·0V. in nitromethane and 4·4V. in nitrobenzene.[67]

The conductivity of an aqueous solution containing 39·4% of lithium bromide has been measured[55] from −70° to 20°C. and the results are shown in Fig. 4.

The theory of the conductivity of aqueous solutions of electrolytes has been extended by introducing the concept of closest approach; complete

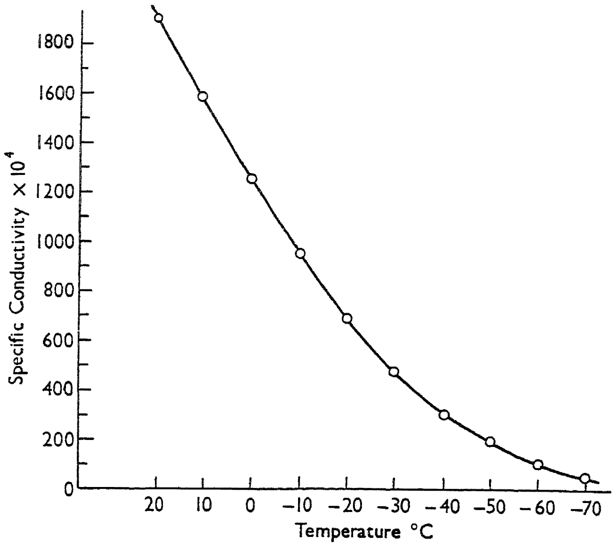

FIG. 4. CONDUCTIVITY OF AN AQUEOUS SOLUTION CONTAINING 39·4% OF LITHIUM BROMIDE

quantitative agreement of the calculated values with experiment is found for lithium bromide and other uni-univalent electrolytes at concentrations less than 0·1N.[59] Lithium bromide is completely dissociated in moderately concentrated aqueous solutions.[30] The field effect in lithium bromide was measured by investigating the variation of conductivity with electric field strength up to 100 kV./cm.; at 100 kV./cm., the percentage increase in conductivity at low field conductivities is 7·3 $ohm^{-1}cm.^{-1}$ [68] For aqueous lithium bromide solutions, the experimental variation of conductivity with concentration, shown in Fig. 5, does not agree with the Debye–Onsager equation; correspondingly the voltage effect is relatively large.[69] The effect of lithium bromide, and of other uni-univalent electrolytes, on the concentration ionization constant of acetic acid in aqueous solutions of ionic strengths 1·0 and 2·7 was determined at 25°C.; it was found that the value of p*K* for acetic acid is an additive quantity dependent separately on each ionic species of the added electrolyte; the Brønsted specific ionic interaction theory fully explains the observed additivity.[70]

Solutions of lithium bromide in molten iodine bromide are poor conductors.[71] The conductivity of lithium bromide in organic solvents has been fairly widely studied. In acetone, conductivity measurements, given in Table XVI, have shown that lithium bromide shows behaviour intermediate between that to be expected for a high degree of dissociation and that for extensive molecular association.[72]

TABLE XVI.- EQUIVALENT CONDUCTIVITY (Λ) OF LITHIUM BROMIDE IN ACETONE

(c = g.-equiv. per litre)

10^4c	0·7663	1·148	1·525	2·057	5·096	7·561	8·025	24·11	33·23
Λ	138·0	132·7	128·0	121·2	100·0	91·52	88·70	62·39	55·51

The dissociation constant of lithium bromide in aqueous acetone was calculated from the conductances of a series of lithium bromide solutions in acetone-water mixtures measured at 25° and 35°C.[73] The dissociation constant of lithium bromide[74] in 90% acetone–10% water is $12{\cdot}0 \times 10^{-3}$. In anhydrous acetic acid solution, the limiting equivalent conductance of lithium bromide is 29 cm.^{2}equiv.$^{-1}$ohm^{-1} and the ion-pair dissociation constant is $7{\cdot}2 \times 10^{-7}$ as determined by conductivity measurements; these and similar data for other substances were used to test the hypothesis that exchange reactions of the type $MBr + M'X \rightleftharpoons M'Br + MX$ (where M = Li, Na or K and M'X = sodium acetate, sodium formate, lithium acetate or lithium formate) occur in acetic acid.[75] To a mixture of lithium bromide and dioxan contained in a conductivity cell, water or ethyl alcohol was added gradually in measured amounts and the volume at which a sharp rise in current occurred was determined; the critical quantities are for water, 2·69 moles per litre of dioxan and for alcohol, 6·36 moles per litre of dioxan; the results are discussed in relation to the mechanism of dissociation of electrolytes.[76] The measured conductivities of solutions of lithium bromide in benzonitrile have been interpreted as showing that, except in extremely dilute solution, lithium bromide is incompletely dissociated.[77] From the measured conductivities in benzonitrile and the dielectric constant of the solvent, the dissociation constant of lithium bromide is calculated to be $3{\cdot}1 \times 10^{-2}$ at 25°C.[78] The measured conductivities of dilute

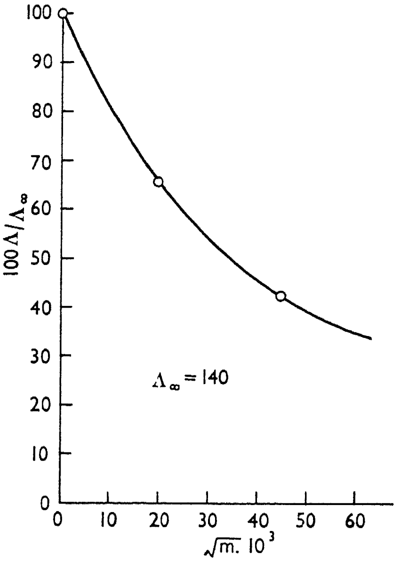

FIG. 5. EQUIVALENT CONDUCTIVITY (Λ) OF AQUEOUS LITHIUM BROMIDE
(m = moles per litre)

solutions of lithium bromide in benzaldehyde are consistent with the square-root rule of Kohlrausch deduced theoretically by Debye and Hückel as a limiting law for dilute solutions.[79] The dissociation constant of lithium bromide in acetophenone is $0{\cdot}92 \times 10^{-4}$ from conductivity measurements.[80] The measured equivalent conductivities of solutions of lithium bromide in *cyclo*-hexanol are not in agreement with the Debye–Hückel–Onsager theory of conductivity in solutions of low dielectric constant.[81] The limiting conductivity, extrapolated from measured conductivities, of lithium bromide in ethyl cyanoacetate is 19·10 and of lithium bromide in *o*-toluonitrile is 27·80; the conductivity of the solutions is a linear function of the square-root of the concentration.[82] The conductivity of solutions of lithium bromide in acetone have been measured with 75-cm. waves; the increase of conductivity with frequency is of an order of magnitude agreeing with the Debye–Falkenhagen theory.[83]

The electrochemistry of mixtures of lithium and aluminium bromides in organic solvents has been investigated;[63,84,85] in ethyl bromide, ethylene bromide, benzene and toluene, the specific conductivity increases with increase in the concentration of lithium bromide; the maximum specific conductivity in ethyl bromide is $12{\cdot}78 \times 10^{-3}$, in benzene $5{\cdot}72 \times 10^{-3}$ and in toluene $5{\cdot}28 \times 10^{-3}$ reciprocal ohms and that in ethylene bromide has also been measured. Electrolysis of lithium bromide–aluminium bromide mixtures in ethyl bromide, benzene, toluene or xylene produces metallic aluminium at the cathode; but if the electrolysis is carried out in nitrobenzene, metallic lithium is deposited. The decomposition potential in ethyl bromide is 2v., in benzene 1·60v., and in toluene 2·00v.

The electrolytic transport of water in 0·1N-lithium bromide solution is 8·15 and the transport number of the lithium ion[86] is 0·401. The transport number of bromide ion in an acetone solution of lithium bromide is 0·833; addition of methanol to the solution causes a sharp decrease in the transport number of bromide ion and hence it is concluded that in acetone lithium bromide forms complexes which are destroyed by methanol.[87]

For lithium bromide the Soret coefficient[88] ($\times 10^4$) is −20; other measurements have shown that the coefficient is temperature dependent and that it can be obtained by the summation of the coefficients of the single ions.[89]

The activity coefficients of lithium bromide at 25°C. have been calculated[64] from the molalities of isopiestic solutions of lithium bromide and calcium chloride and from the molalities of isopiestic solutions of lithium bromide and sulphuric acid; the results are given in Table XVII.

TABLE XVII.- ACTIVITY COEFFICIENT (γ) OF LITHIUM BROMIDE AT 25°C.

(m = molality of solution)

m	γ	m	γ	m	γ
0·1	0·796	1·6	0·917	9·0	12·92
0·2	0·766	1·8	0·964	10·0	19·92
0·3	0·756	2·0	1·015	11·0	31·0
0·4	0·752	2·5	1·161	12·0	46·3
0·5	0·753	3·0	1·341	13·0	70·6
0·6	0·758	3·5	1·584	14·0	104·7
0·7	0·767	4·0	1·897	15·0	146·0
0·8	0·777	4·5	2·28	16·0	198·0
0·9	0·789	5·0	2·74	17·0	260
1·0	0·803	6·0	3·92	18·0	331
1·2	0·837	7·0	5·76	19·0	411
1·4	0·874	8·0	8·61	20·0	485

The concentration-dependence of the activity coefficient of aqueous lithium bromide solutions was calculated using a modified Debye-Hückel theory and found to agree with experimental data.[30] In lithium bromide solutions, the ionic activity coefficient of water, calculated from e.m.f. measurements, varied between 0·999 and 0·942 in the concentrations studied and is slightly lower than in lithium chloride solutions.[90] The measured activity coefficient of ethyl acetate in aqueous lithium bromide solution is in fairly good semi-quantitative agreement with that calculated using a modified Debye–McAulay-type equation and that calculated using the Debye equation.[91]

Lithium bromide increases the rate of hydrolysis of benzoyl chloride in aqueous acetone at 25°C.;[92] for approximately 0·03N-lithium bromide, the rate increase in 5% water – 95% acetone is 175%, that in 10% water – 90% acetone is 40% and that in 15% water – 85% acetone is 15%; in 15% water –

85% acetone, the rate increase for 0·013N-lithium bromide is 8·3 and that for 0·045N-lithium bromide is 18%. Lithium bromide increases the rate of hydrolysis of *tert.*-butyl bromide in 10% water - 90% acetone at 25°C.;[74] the effect on k°, the rate constant at zero ionic strength, is given in Table XVIII.

TABLE XVIII.- EFFECT OF LITHIUM BROMIDE ON RATE OF HYDROLYSIS OF *tert.*-BUTYL BROMIDE AT 25°C.

Molarity of LiBr	0·000	0·024	0·046	0·106
$10^5 k^{\circ}$	1·25 ± 0·02	1·36 ± 0·03	1·42 ± 0·04	approx. 25

Lithium bromide in acetone has been used in a demonstration of bimolecular anionotropic change.[93]

The adsorption by precipitated lead sulphide of lithium bromide from solutions saturated with lead sulphide and lead sulphate has been studied and discussed in relation to the compatibility of the space lattices.[94] The coagulation concentration of lithium bromide for sulphur sols was measured and discussed.[95] Electrophoresis was studied in solutions of poly-4-vinyl-N-butylpyridinium bromide with added lithium bromide.[96] An appreciable Donnan membrane effect found with solutions of polymethacrylic acid in ethanol is eliminated by addition of lithium bromide.[97]

Chemical Properties

Lithium bromide does not react with dry air at 560°C.; it is not hydrolysed at its melting point (547°C.) but at about 560°C. it reacts with a mixture of steam and oxygen to give bromine.[98] Lithium bromide accelerates the reaction of solid potassium chlorate with graphite and with Nuchar and causes mixtures of potassium chlorate and charcoal black to ignite at 343°C.[99] Electrolysis of lithium bromide in anhydrous acetic acid using a silver anode results in the formation of silver bromide in quantitative yield.[100] The compound CCl_3SO_2Cl rapidly liberates bromine from lithium bromide in acetone; triphenyl methyl chloride, Ph_3CCl, has no action on lithium bromide in acetone.[101] The action of lithium bromide on esters of phosphorous acid has been studied; with esters of the general formula $(RO)_3P$, the products are RBr and $(RO)_2POLi$; with the dibutyl ester of phosphorous acid, $(BuO)_2POH$, the products are butyl bromide and a compound of formula $C_8H_{18}O_3PLi$; with the diethyl ester of phosphorous acid, $(EtO)_2POH$, an unidentified compound is formed which contains halogen and 18·2–18·6% of phosphorus.[102] The presence of lithium bromide markedly increased the thermal instability of amylsodium and, alone among the alkali halides, resulted in the formation of diamyl alcohol, triamyl-carbinol and a hexadecene as decomposition products.[103] Reaction of the 1:2 addition compound of tetraphenyl lithium borohydride, $Li(BPh_4)$, and lithium bromide, $Li(BPh_4),2LiBr$, with mercury in chloroform yields some phenyl mercuric chloride.[104]

The existence of the complex tetrabromo-cobalt (II) ion, $[CoBr_4]^{-2}$, in butyl alcohol solutions of cobalt (II) perchlorate and lithium bromide has been shown spectrophotometrically.[105] Spectrophotometric measurements have also shown that, in ethanol solution, bromide ion, added as lithium bromide, displaces chloride ion from the complex tetrachloro-cobalt (II) ion, $[CoCl_4]^{-2}$, more readily than does iodide ion, added as lithium iodide.[106]

The 1:2:2 addition compound of lithium bromide, aluminium bromide and nitrobenzene, $LiBr,2AlBr_3,2PhNO_2$, has been prepared and its properties examined.[107] β-Alanine, $H_2NCH_2CH_2CO_2H$, gives with lithium bromide the addition compound $H_2NCH_2CH_2CO_2H,LiBr,1\,5H_2O$.[108]

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Dehydrobromination of the 4-Br derivative of 17α-hydroxy-21-acetoxypregnane-3,11,20-trione has been accomplished by using lithium bromide (*a*) in formylpiperidine and (*b*) in dimethylacetamide.[109] Methyl triphenyl phosphonium bromide, Ph_3PMeBr, in ether with phenyl lithium, PhLi, under nitrogen gave triphenylphosphine methylene, $Ph_3P{:}CH_2$, which was kept in solution and treated with benzophenone in ether giving[110] a lithium bromide adduct of the compound $Ph_3P^+ \rightarrow O^-$. The kinetics of the exchange of radioactive bromide ion (from radioactive lithium bromide) with substituted phenyl and benzyl bromides have been studied.[111] The isotopic exchange reactions between radioactive lithium bromide and *iso*propyl bromide and *tert.*-butyl bromide in anhydrous acetone have also been studied.[112]

Applications

Aqueous solutions of lithium bromide can be used in air conditioning,[113] in the dehydration of moist acid-containing gases[114] and in the dehydration of mineral oil.[115] Fused lithium bromide can be used in a flux for melting magnesium-lithium alloys[116] and in the electrolyte for a primary cell.[117] The effect of lithium bromide on cellulose dispergation has been studied.[118]

Analytical

In connection with the analytical control of pharmaceutical materials it was shown that 50 parts of sulphate in 100,000 parts of lithium bromide could be detected turbidimetrically.[119]

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SECTION XIII

LITHIUM IODIDE

By W. P. DOYLE

Preparation

Lithium iodide has been prepared by the action of iodine on lithium hydride in ether solution; the method is rapid, practically quantitative, yields a pure product and is almost certainly suitable for other metallic iodides of groups I and II.[1] A similar method, having the same advantages but actually applied only to barium iodide, depends on the reaction of the metallic hydride with ammonium iodide in pyridine.[1] To ensure the stability of lithium iodide, it is recommended[2] that, after preparation, the salt be fused in a quartz vessel at 245–63° C.

Physical Properties

The crystal structure of lithium iodide has been determined;[3] it possesses the rock-salt structure and the interatomic distance is 3·03 A. A later *X*-ray powder analysis confirms[4] the rock-salt structure but gives the interatomic distance as 3·537 A. The discrepancy between the two determinations has been discussed and it is suggested that the material used in the later determination was probably not anhydrous.[5] The crystal structure of lithium iodide trihydrate, $LiI,3H_2O$, has been determined[6] and confirmed.[7] The unit cell is hexagonal and contains two molecules. The spacings are: $d_{110} = 7{\cdot}45$ A.; $d_{001} = 5{\cdot}45$ A. The space group is *6e* – 4. *X*-Ray diffraction studies of aqueous lithium iodide solutions show a broad ring, the position of which is independent of concentration; the ring is ascribed mainly to interference between the scattering from the iodide ion and that of the surrounding water molecules.[8]

The lattice energy of lithium iodide is, from mass spectral studies, 174·0 kg.-cal. per mole.[9] An investigation of the anode ray emission of lithium iodide confirmed the lithium line at 2934·1 A. previously observed and established a general correspondence with the helium spectrum.[10] The frequency of the lattice oscillations of lithium iodide has been calculated, on the basis of the Born model, to be $6{\cdot}7 \times 10^{12}$; the unharmonicity was also calculated.[11] The density effect for the ionization losses of charged particles was calculated using a dispersion model.[12] The dielectric constant, determined experimentally,[13] is 8·2 and the value calculated theoretically is in good agreement with lattice energy data.[14] The photoelectric effect of a solution of lithium iodide, measured by a spark counter, is large and is linearly related to the concentration of the solution.[15]

The cubic compressibility of lithium iodide has been reported[16] as 7·2 per megabar × 10^{-6}. Later compressibility measurements,[17] over the pressure range 12000 kg.cm.$^{-2}$, showed that at 30°C. the cubic compressibility of anhydrous lithium iodide is represented by the equation:

$$-\Delta V/V_0 = 58{\cdot}89 \times 10^{-7}\, p - 107{\cdot}4 \times 10^{-12}\, p^2,$$

and that of the trihydrate, assuming equal compressibility in all directions, by the equation:

$$-\Delta V/V_0 = 65{\cdot}1 \times 10^{-7}\, p - 117 \times 10^{-12}\, p^2.$$

The compressibility calculated on the basis of the theory of the grating[18] is qualitatively consistent with the experimental data.[16] For aqueous solutions of lithium iodide of various concentrations, compressibilities up to 1000 bars have been determined[19] at 25°C. and are given in Table I where x_1 is the weight fraction of water in the solution, x_2 is the weight fraction of lithium iodide in the solution and $-\Delta pv$ is the specific compression of a solution for an increase of pressure from 1 to 1000 bars.

TABLE I.- COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF LITHIUM IODIDE

100 x_2	0·00	9·62	25·58	33·87	46·37	53·33
$-\Delta pv/x_1 \times 10^4$	394·6	386·9	375·7	370·2	363·8	362·5

The heat of sublimation of lithium iodide is calculated[20] as between 15 and 35 using a previously developed equation[21] relating thermochemical properties to lattice structure. The partial heats of sublimation to monomer and dimer at 0° abs. are 44·9 and 45·5 kg.-cal. per mole respectively, as determined from mass spectral measurements.[9] The heat of dissociation of dimeric vapour, $(LiI)_2$, into monomeric vapour, LiI, is 44·4 kg.-cal. per mole;[9] the heat of dissociation of the monomeric vapour is 78·8 kg.-cal. per mole as determined from electron impact appearance potentials, and 88·0 kg.-cal. per mole, as determined from optical studies.[9]

The sum of the standard free energies of hydration of lithium and iodide ions was, from standard electrode potential and other data, calculated as 177·9 kg.-cal. per mole.[22] The total heat of hydration of lithium iodide has, from measurements of heat of solution and the value of the lattice energy, been critically selected as 184 kg.-cal. per mole; this value was used to obtain the heat of hydration of the simple lithium ion, Li^+, 121 kg.-cal. per g. ion, and of the simple iodide ion, I^-, 63 kg.-cal. per g. ion; the results are discussed in relation to the nature of the hydration sphere.[23] The heat of hydration of anhydrous lithium iodide to the hemi-hydrate ($LiI \rightarrow LiI,0{\cdot}5H_2O$) is 10·1 kg.-cal., of the hemi-hydrate to the monohydrate ($LiI,0{\cdot}5H_2O \rightarrow LiI,H_2O$) 9·3 kg.-cal., of the monohydrate to the dihydrate ($LiI,H_2O \rightarrow LiI,2H_2O$) 16·4 kg.-cal., and of the dihydrate to the trihydrate ($LiI,2H_2O \rightarrow LiI,3H_2O$) 16·0 kg.-cal. per mole.[24] The limit of full solvation has been measured and discussed in relation to the structure of concentrated solutions of lithium iodide.[25] Information about the hydration of the ions in a concentrated solution of lithium iodide has been derived from vapour pressure data.[26]

The apparent molal heat capacity, and hence the partial molal heat capacity, of lithium iodide in aqueous solution have been related to the concentration of the solution.[27]

Four hydrates of lithium iodide have been observed, $LiI,0{\cdot}5H_2O$, LiI,H_2O, $LiI,2H_2O$ and $LiI,3H_2O$; the congruent melting point of the monohydrate is 131°C. or higher, that of the dihydrate is 79°C. and that of the trihydrate is[24] 75°C. The solubility of lithium iodide in nitrobenzene is 5·27 ± 0·04% at 250°C.; the distribution ratio of lithium iodide between water and nitrobenzene varies from 3250 to >6830 as the concentration of lithium iodide in the water layer decreases from 42·2 to 10·1 g. of lithium iodide per 100 g. of solution.[28] The solubilities of lithium iodide in methanol, acetonitrile and formic acid have been determined at 18° and 25°C.; the results are given in Table II.[29] Distribution ratios for lithium iodide and lithium iodide–ammonium iodide mixtures between ethylene glycol and ethyl acetate were determined[30] at 30°C. Aqueous lithium iodide solutions can dissolve urea–formaldehyde resins.[31]

TABLE II.- SOLUBILITY OF LITHIUM IODIDE IN METHANOL, ACETONITRILE AND FORMIC ACID

Solvent	t°C.	S (g./100 g. of solvent)
Methanol	18 25	143 171
Acetonitrile	18 25	147 154
Formic acid	18 25	139 146

The theory of the viscosity of electrolyte solutions has been extended by introducing the concept of closest approach, but comparison of the values calculated for lithium iodide and other uni-univalent electrolytes with the experimental values shows that the treatment gives no improvement on the older theory.[32]

The freezing point constant at zero concentration of lithium iodide dissolved in calcium chloride hexahydrate, $CaCl_2,6H_2O$, has been determined as 66·4 and its significance discussed.[33] The vapour pressures of aqueous solutions of lithium iodide relative to those of potassium chloride solutions have been determined[34] by an isopiestic method; the results are given in Table III where m_1 is the molar concentration of the potassium chloride solution and m_2 that of the isopiestic solution of lithium iodide.

TABLE III.- ISOPIESTIC AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE AND LITHIUM IODIDE

m_1	m_2	m_1	m_2	m_1	m_2
0·1235	0·1197	1·160	0·9705	2·720	2·018
0·1561	0·1491	1·167	0·9782	2·854	2·089
0·1714	0·1630	1·238	1·026	2·909	2·127
0·1976	0·1866	1·334	1·098	2·974	2·170
0·2034	0·1910	1·616	1·294	3·245	2·327
0·2055	0·1941	1·757	1·392	3·596	2·529
0·2646	0·2485	1·825	1·443	3·942	2·710
0·2819	0·2627	2·079	1·613	4·183	2·832
0·5751	0·5176	2·536	1·906	4·198	2·845
0·7848	0·6877	2·625	1·956	4·522	3·012
0·7964	0·6852			4·81	3·152

The molecular weight of lithium iodide in nitrobenzene varies from 270 to 365; the formula weight of lithium iodide, LiI, is 133·86, hence the 270 value is approximately double and is evidence that lithium iodide polymerizes in nitrobenzene.[28]

The decomposition potential of fused lithium iodide is 2·48 V. and this experimental value agrees with those calculated by two different methods.[35]

The theory of the electrical conductivity of aqueous solutions of electrolytes has been extended by introducing the concept of closest approach; complete quantitative agreement of the calculated values with experiment is found for lithium iodide and other uni-univalent electrolytes at concentrations less than 0·1 N.[32] The molar conductivity of aqueous solutions of lithium iodide has been measured.[36] The conductivities of solutions of various concentrations of lithium iodide in iodine were measured at various temperatures; the specific conductivity increases with concentration of the iodide and reaches a maximum of $1{\cdot}1 \times 10^{-1}$ ohm^{-1} cm.$^{-1}$ at 130°C.; the molar conductivity of a

24·16% solution of lithium iodide at 130° is 13·66 cm.^{2} mole^{-1} ohm^{-1}; the temperature coefficient of the specific conductivity is negative at small concentrations of lithium iodide and becomes positive at higher concentrations; the conductivity of iodide solutions in iodine is conditioned by the polymerization of polyiodides, the polymers dissociating electrolytically,[37] *e.g.*:-

$$(LiI_3)_2 \rightleftharpoons Li^+ + LiI_6^- \text{ or}$$
$$(LiI_3)_2 \rightleftharpoons I^- + Li_2I_5^+.$$

The conductivities at 4°, 15° and 25°C. of solutions of lithium iodide in ethyl alcohol have been measured; values of the equivalent conductivity are given in Table IV and of the limiting conductivity and dissociation constant in Table V; the mean heat of dissociation was calculated as 12·9 kg.-cal. from 4° to 15°C. and as 5·8 kg.-cal. from 15 to 25°C.[38]

TABLE IV.- EQUIVALENT CONDUCTIVITY (Λ) OF LITHIUM IODIDE IN ETHYL ALCOHOL (c = g.-equivs. per litre)

4°C.		15°C.		25°C.	
$c \times 10^4$	Λ	$c \times 10^4$	Λ	$c \times 10^4$	Λ
1·1264	27·92	1·0970	34·85	1·1351	42·24
2·6993	27·40	2·5061	34·22	2·4221	41·52
4·7472	26·87	4·3794	33·56	4·3912	40·65
7·0501	26·41	6·7438	32·69	7·4247	39·65
9·7752	25·97	9·9376	32·26	10·5459	38·88
13·5582	25·48	13·4454	31·68	13·9890	38·15

TABLE V. - LIMITING CONDUCTIVITY AND DISSOCIATION CONSTANT OF LITHIUM IODIDE IN ETHYL ALCOHOL

t°C.	Limiting Conductivity	Dissociation Constant
4	28·92	0·412
15	36·08	0·172
25	43·80	0·121

The conductivities at 25°C. of lithium iodide in 0·0001–0·002N-nitromethane solutions have been measured and the limiting conductivity was found to be 117·5; the deviation of this value from the value calculated from the Debye-Hückel-Onsager equation is ascribed to ionic association of lithium iodide in nitromethane.[39] The conductivities of solutions of lithium iodide in benzonitrile have been measured[40] at 0°, 25° and 50°C.; the results, which are given in Table VI, are interpreted as showing that, except in extremely dilute solution, lithium iodide is incompletely dissociated. From the measured conductivities in benzonitrile and the dielectric constant of the solvent, the dissociation

TABLE VI.- EQUIVALENT CONDUCTIVITY OF LITHIUM IODIDE IN BENZONITRILE (v = dilution in litres)

v	0°C.	25°C.	50°C.
100	15·36	24·73	34·25
500	17·88	34·54	48·57
1,000	23·57	38·45	54·10
2,000	25·57	41·22	58·08
5,000	27·23	43·38	61·09
10,000	27·96	44·35	62·38

constant of lithium iodide is calculated[41] to be 8×10^{-3} at 25°C. The conductivities of 0·0005 N. to 0·1 N. solutions of lithium iodide in furfural indicate that furfural is a solvent possessing high dissociating power and the degree of solvation of the salt cation is approximately of the same order of magnitude as in aqueous solution.[42] In methyl cyanide, lithium iodide is a strong electrolyte.[43] The electrical conduction of the vapour of lithium iodide has been studied.[44]

The Soret coefficient of lithium iodide, as measured in a diffusion apparatus, is $-2{\cdot}3 \pm 0{\cdot}2$ milliunits per degree;[45] similar measurements gave the coefficient as $-1{\cdot}35 \times 10^{-3}$ at 30°C. increasing to $0{\cdot}42 \times 10^{-3}$ at 60°C. and show that the coefficient is temperature-dependent;[46] the Soret coefficient of lithium iodide, and of other uni-univalent electrolytes, can be obtained by the summation of the coefficients of the single ions.[45,46]

The activity coefficient of lithium iodide in aqueous solution has been determined from vapour pressure measurements as between 0·8 and 1·7 in the concentrations studied[34] and the stoicheiometric activity coefficient has been derived from distribution studies.[30]

Lithium iodide is a very effective catalyst for the mutarotation of glucose in pyridine solution.[47] The reversible S_N2 reaction, alicyclic bromide + I^- = alicyclic iodide + Br^-, has been studied using lithium iodide in anhydrous acetone.[48]

The difference in the dipole moments of ^{6}LiI and ^{7}LiI, due to isotopic substitution, is $2{\cdot}6 \times 10^{-21}$ millidebyes.[49] The mass spectrum of lithium iodide has been determined[9] at 700° abs.; the appearance potentials for the major ions in the spectrum are presented in Table VII.

TABLE VII.- APPEARANCE POTENTIALS IN MASS SPECTRUM OF LITHIUM IODIDE

m/e	Ion	Appearance potential in electron volts
134	$^7LiI^+$	8·55 ± 0·15
141	$^7Li_2I^+$	8·75 ± 0·10
7	Li^+	9·2 ± 0·15
7	Li^+	11·75 ± 0·20
127	I^+	14·5 ± 0·20

Chemical Properties

When anhydrous lithium iodide is heated in pure dry oxygen, iodine is liberated and lithium oxide and iodate are formed.[50] Electrolysis of lithium iodide in anhydrous acetic acid using a silver anode results in the formation of silver iodide in quantitative yield.[51]

Spectrophotometric measurements on butyl alcohol solutions containing lithium iodide and cobalt (II) perchlorate have shown the existence of the complex cobalt (II) pentaiodide ion, $[CoI_5]^{-3}$, which on dilution dissociates to form the complex cobalt (II) tetraiodide ion, $[CoI_4]^{-2}$.[52] Similar spectrophotometric measurements have shown that in ethyl alcohol solution iodide ion, added as lithium iodide, displaces chloride ion from the complex cobalt (II) tetrachloride ion, $[CoCl_4]^{-2}$, less readily than does bromide ion, added as lithium bromide.[53]

β-Alanine, $H_2NCH_2{\cdot}CH_2{\cdot}CO_2H$, gives two addition compounds with lithium iodide:

$$H_2NCH_2{\cdot}CH_2{\cdot}CO_2H,\ LiI, 1{\cdot}5H_2O;$$
$$\text{and } 2H_2NCH_2{\cdot}CH_2{\cdot}CO_2H, LiI, 1{\cdot}5H_2O.$$[54]

Refs. p. 236

The 1:1 co-ordination complex of lithium iodide and dimethyl formamide, LiI,HCON$(CH_3)_2$, has been prepared and its properties studied.[55]

Lithium iodide in methyl cyanide exchanges iodine with butyl iodide; the process involves the iodide ion, I .[43]

Nessler reagent prepared with lithium iodide instead of potassium iodide is extremely sensitive.[56]

Examination of the system PbI_2–LiI–H_2O shows that the only double salt is PbI_2,LiI,$4H_2O$,[57] although at higher temperatures there are indications of a double salt containing less water.[58] The effect of lithium iodide on the solubility of thallium iodide in various solvents was studied and found to give rise to the double salt $LiTlI_4$.[59] Mixed crystals of lithium iodide and sodium sulphate have been prepared containing from 0–0·57% of iodine.[60]

Applications

Lithium iodide has been used as a constituent of disinfectants.[61] The effect of lithium iodide on cellulose dispergation has been studied.[62]

Lithium iodide has been used to effect dehydrobromination of the 4-Br derivative of 17α-hydroxy-21-acetoxypregnane-3,11,20-trione in dimethylformamide.[55]

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SECTION XIV

LITHIUM SULPHIDE

By C.W. GROGAN

Lithium sulphide is prepared from the hydrosulphide (see below). When the alcohol–hydrosulphide complex is rapidly heated to 360°C. *in vacuo*, both lithium sulphide and lithium ethoxide are formed, and on passing a stream of gas containing 90% of hydrogen and 10% of hydrogen sulphide over the residue at 120°C., lithium hydrosulphide is formed. If this is heated to 360°C. in the presence of solid potassium hydroxide and phosphorus pentoxide, nearly pure lithium sulphide is formed. The disulphide is also prepared by the addition of sulphur to an alcoholic solution of the hydrosulphide.[1]

Other methods employed for the preparation of the sulphide include direct synthesis from sulphur and lithium in liquid ammonia, and the reduction of lithium sulphate monohydrate by hydrogen in the silent electric discharge, according to the equation:-

$$Li_2SO_4 + 4H_2 \rightarrow Li_2S + 4H_2O$$ [2-5]

Lithium sulphide has a calcium fluoride structure, with a lattice constant = 5·708 A. determined by the powder method.[3]

Lithium sulphide has been used in the preparation of electroluminescent materials, in the formation of corrosion inhibitors for steels in contact with hydrocarbon oils and in the preparation of mixed alkyl-alicyclic disulphides.[6-8]

Lithium hydrogen sulphide.

Lithium hydrogen sulphide has been prepared by the action of hydrogen sulphide on lithium ethoxide. The ethoxide is prepared by the action of lithium chloride solution in alcohol on an alcoholic solution of sodium ethoxide, the precipitated sodium chloride being filtered off under hydrogen and the lithium ethoxide isolated by evaporating the solution at 70°C. The action of hydrogen sulphide on the alcoholate in dry ether forms 2LiHS,EtOH as a very deliquescent, pure white powder which is decomposed rapidly by carbon dioxide. The molecule of alcohol cannot be removed without causing the decomposition of the hydrosulphide. Pure lithium hydrosulphide can be prepared by the action of hydrogen sulphide on lithium in dry ether, the purity of the metal being the limiting factor.[9]

By replacing the lithium ethoxide by lithium amyloxide in ether and passing a slow stream of hydrogen sulphide, a colourless precipitate turning yellow in air is obtained. It decomposes at 50°C. *in vacuo*. It has a tetragonal structure with $a = 5{\cdot}54$, $c = 12{\cdot}31$kX. and there are 8 mols. per unit cell. The following data were obtained:-[10] $d_{25^\circ} = 1{\cdot}38$. Heat of solution $\Delta H = 8{\cdot}5$kg.-cal./mol. Heat of formation $\Delta H = -60$kg.-cal./mol. For $2LiOH + H_2S = Li_2S + H_2O$ $\Delta H = 6{\cdot}4$kg.-cal./mol.

Lithium polysulphides.

Four routes have been explored for the preparation of these polysulphides:-

(1) The action of sulphur on lithium sulphide in alcohol, aqueous alcohol, and aqueous solutions resulting in solutions containing polysulphides which cannot be crystallized.

(2) The action of sulphur on lithium hydrosulphide in anhydrous alcohol; the primary product is lithium tetrasulphide (Li_2S_4), provided that the sulphur is present in the quantity required by the equation:-

$$2LiHS + 3S \rightarrow Li_2S_4 + H_2S$$

The ethyl alcohol complex $Li_2S_4,2C_2H_5OH$ crystallizes from the solution at room temperature while at the boiling point Li_2S_2,C_2H_5OH is obtained. When lesser proportions of sulphur are used a mixture of Li_2S_4 and LiHS results.

(3) The action of sulphur on dry lithium carbonate or hydroxide.[11] This yields polysulphides and higher oxidation products, e.g. - at 200°C. - thiosulphate and polysulphide; at 400°C. - some sulphur and thiosulphate; at 700°C. - polysulphide and sulphate together with small quantities of thiosulphate and sulphite.

(4) The action of sulphur on molten lithium. Here there is no reaction until 0·5g.-atom of sulphur has been added to 1g.-atom of lithium, when an explosive reaction occurs, forming lithium sulphide and small quantities of polysulphide. A study of the lithium sulphide-sulphur system shows that at atmospheric pressure only lithium sulphide (Li_2S), (stable at its m.p. 900°-975°C.) and lithium disulphide (Li_2S_2) (slightly decomposed at its m.p. 369·5°C.) are stable.[12]

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SECTION XV

LITHIUM SULPHATE

By C.W. GROGAN

Recent studies on the preparation of pure lithium sulphate have shown that the addition of ethyl alcohol to solutions acidified with dilute hydrochloric acid precipitates the pure salt,[1] while the solubility isotherm for the ternary system $LiCl-Li_2SO_4-H_2O$ indicates that the sulphate is precipitated quantitatively from lithium chloride solution.[2] It is also insoluble in liquid ammonia.[3]

Large crystals of lithium sulphate may be grown under controlled conditions of pH. Initial growth of a seed crystal in a solution of pH 4–5 is followed by further growth at pH 6–7 which develops the crystal lengthwise. At fixed temperatures, crystals 3–4in. long have been grown in about four weeks. These are very liable to have flaws.[4–6] The incidence of twinning and the mechanism of spiral growth of such crystals have been investigated.[7]

The isotopic assay of lithium may be carried out by measuring the intensity of selected lithium hydride bands for ^6LiH and ^7LiH when lithium sulphate samples are subjected to low current d.c. arc excitation in an atmosphere of 50% helium and 50% hydrogen.[8]

The crystal structure of lithium sulphate has been established from a number of investigations involving Laue and rotation photographs; measurements of nuclear magnetic resonance have defined the position of the water molecules in the crystalline hydrate.

From the Laue and oscillation photographs on the anhydrous salt, the monoclinic unit cell contains four molecules, the constants being: $a = 8{\cdot}25$A., $b = 4{\cdot}95$A., $c = 8{\cdot}44$A., and $\beta = 107°54'$. The sulphate groups form regular tetrahedra with the sulphur-oxygen distance 1·50A., and the oxygen-oxygen distance 2·45A.; each lithium atom is surrounded by four oxygen atoms each from a sulphate group, forming a nearly regular tetrahedron, with the average lithium–oxygen distance 1·97A., and oxygen-oxygen distance 3·20A.[9]

In the crystalline hydrate (Li_2SO_4,H_2O), the monoclinic unit cell contains two molecules with $a = 5{\cdot}43$A., $b = 4{\cdot}8$A., $c = 8{\cdot}14$A., and $\beta = 107°35'$ with the oxygen of the water molecule at one corner of an oxygen tetrahedron surrounding the lithium atom. The H–O–H angle is 108° and the sulphur-oxygen bonds substantially the same as in the anhydrous salt.[10,11]

In a determination of the crystalline structure of the hydrate employing nuclear magnetic resonance methods on powders and single crystals, measurements of the fine structure of the absorption spectrum in the high frequency region are related to distortion of the water molecules. The hydrogen atoms are 1·57 ± 0·02A. apart on a line making an angle of 46° ± 2 with the binary axis of the crystal.[12,13]

In a more recent determination of the magnetic resonance of a single monohydrate crystal, the H–H distance is 1·59A. If the O–H distance is assumed to be 0·99A., the H–O–H angle will be 106°50'. From the O–O distance measured however, such a value for the H–O–H angle seems unlikely, and an O–H distance nearer to that in water vapour than to that in ice is suggested, when the H–O–H angle becomes 112°40'.[14]

Since a correlation has been observed between hydrogen bonding and an increase in molar volume on replacing hydrogen by deuterium in the hydrate, the figures given in Table I for lithium sulphate hydrate and deuterate are interesting, since they give only negative evidence for the existence of such bonds. It is concluded, however, that absence of expansion when D_2O replaces H_2O does not necessarily imply absence of hydrogen bonding.[15]

TABLE I.- DENSITY AND MOLAR VOLUME OF LITHIUM SULPHATE HYDRATE AND DEUTERATE

	d_4^{20}	Molar Vol.
Li_2SO_4,H_2O	2·051	62·2
Li_2SO_4,D_2O	2·127	61·1

Many studies of the solubility and of the vapour pressure of lithium sulphate have been made, and results are summarised in Tables II and III.

TABLE II.- SOLUBILITY OF LITHIUM SULPHATE IN WATER[16,17]

Temp. °C.	Solubility[16]	Temp. °C.	Solubility[17]
−16	27·32	142·5	22·65
0·6	26·51	186	22·7
19·6	25·85	214	23·0
103	23·72		

TABLE III.- VAPOUR PRESSURE OF LITHIUM SULPHATE SOLUTIONS[18]

Temp. °C.	V.p., mm. Hg	Temp. °C.	V.p., mm. Hg
25·3	20·85	89·65	458·0
30·65	28·5	99·50	657·7
45·65	64·5	100·1	676·4
60·15	129·6	105·25	799·0
69·4	197·3	110·35	945·7
84·3	349·9		

The monohydrate is stable down to −8°C., but at lower temperatures there is a possibility that a dihydrate exists.[16] For the system lithium sulphate-water, the transition temperature of the reaction $Li_2SO_4,H_2O \rightarrow Li_2SO_4 + H_2O$ occurs at 232·8°C. and 26·7atm.[17] A thermal analysis of the hydrate shows a loss of water at about 210°C., a large endothermic effect at 600°C., presumably due to an inversion, and the m.p. at 880°C.[19]

Measurements of the integral heat of dilution (L) of 1/g. equiv. of lithium sulphate in hydrochloric acid of varying concentration have been made during a study of the hydration of the ions of the alkali metals. For lithium the coordination number is almost 3·8, nearly the same as that of water.

The value dL/dm (where m is the concentration of hydrochloric acid in the individual solution - 50mols. H_2O + m mols. HCl) is approximately constant between m = 0·84 and 3·51.[20] For aqueous solutions between 10^{-1} and 10^{-4}M., the integral heats of dilution V_m, and differential heats of dilution Φ_m (m = molar concentration) are positive at the highest dilution, but pass through a maximum when m is still very small and ultimately become negative with further rise in m.[21]

Thermodynamic data for lithium sulphate have been extensively studied and values of $\Delta H°$, $\Delta F°$, and $\Delta S°$ are given for the synthesis of lithium sulphate and for the heat of formation of the hydrate.

From measurements at 20–30°C., of the E.M.F. of the reversible cell

$$\text{Li-Hg } (0·035\%) \mid Li_2SO_4,H_2O \text{ (satd. soln.) } Hg_2SO_4 \mid \text{Hg},$$

$$E = 2·67489 - 0·000241\,(t - 25) \text{ volts.}^{22}$$

and for the reaction, $2Li_{(s)} + S_{(s,\alpha)} + 2O_{2(g)} \rightarrow Li_2SO_{4(s)}$, at 25°

$$\Delta H^\circ_{298\cdot1} = -338099\text{g.-cal.}$$
$$\Delta F^\circ_{298\cdot1} = -313614\text{g.-cal.}$$
$$\Delta S^\circ_{298\cdot1} = -82\cdot3\text{g.-cal./}^\circ\text{C.}$$
$$S^\circ_{298\cdot1} = 38\cdot7\text{g.-cal./}^\circ\text{C./mol.}$$

These values were confirmed in a later determination[23] and extended to cover the range 360°-1270°K.[24]

e.g. Heat of conversion at 859°K. = 6530·7g.-cal./mol.
Heat of melting at 1133°K.(m.p.) = 1833·0g.-cal./mol.
Entropy of melting = 1·6g.cal./mol./degree.

For the reaction $Li_2SO_{4\,(s)} + H_2O \rightarrow Li_2SO_4,H_2O$, at room temperature,

$$\Delta H = -3018\text{g.-cal.}$$

and the vapour pressure of the hydrate at 298·1°K. is $9\cdot21 \times 10^{-3}$atm.

Thus $\Delta F^\circ_{298\cdot1}$ for $H_2O_{(g)} = -2775$g.-cal. and for $H_2O_{(l)} = -721$g.-cal.[23]

As is shown in Tables IV and V the conductivity of lithium sulphate in aqueous and acidic media has been studied; the degree of dissociation of the salt has also been evaluated, and evidence obtained for the existence of the bisulphate ion.

The dissociation constant for $LiSO_4^-$ is 0·229.[25]

TABLE IV.- SPECIFIC CONDUCTIVITY OF AQUEOUS LITHIUM SULPHATE AT 25°C.[26]

Concentration(M)	Conductivity(κ)	Concentration(M)	Conductivity(κ)
0·003928	0·00080882	0·12701	0·017224
0·019680	0·0035167	0·24602	0·028902
0·053930	0·0084570	0·53770	0·050041

TABLE V.- EQUIVALENT CONDUCTIVITY OF LITHIUM HYDROGEN SULPHATE

Concentration, N.	100κ	Λ
0·1	1·52	152
0·2	2·17	108
0·4	3·37	84·2
0·6	4·24	70·7
0·8	4·80	60·0
1·0	5·33	53·3
1·2	5·57	46·4
1·4	5·80	41·4

The conclusion is reached that the solution of lithium sulphate in sulphuric acid yields one HSO_4^- ion per mol. and since the equivalent conductivity of the cation is low, the decreasing conductivity with increasing concentration is due to interferences with a chain mechanism of conduction by HSO_4^-, since an increase in the bisulphate ion concentration increases the chance of two chains interfering with one another. The solvation of the cation also reduces the freedom of motion of some solvent molecules.[27] An extension of the work to include measurements of viscosity and density in sulphuric acid solutions confirmed the solvation number of Li^+ as 3 and showed that both the density and the viscosity of the solutions increase proportionally with concentration up to 1·8 molal.[28]

In the presence of high concentration of cane sugar the conductivity-concentration relationship of lithium sulphate solutions showed high mobilities for the cation and this is attributed to the decrease in ion radius due to the lower degree of hydration of the ion.[29]

The activity coefficients of lithium sulphate and of lithium hydroxide and sulphuric acid in lithium sulphate solutions have been determined and compared with theoretical values.[30] Confirmation of these results has also been obtained from isopiestic measurements with solutions of potassium chloride.[31]

The cell,

$$\mathrm{Hg} \mid \mathrm{Hg_2SO_4} \mid \mathrm{Li_2SO_{4(c)}} \mid \mathrm{LiHg} \mid \mathrm{Li_2SO_{4(c_1)}} \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg},$$

where c_1 is the reference and c the salt concentration, avoids liquid junction potentials and gave the results shown in Table VI.

TABLE VI.- ACTIVITY COEFFICIENTS FOR LITHIUM SULPHATE SOLUTION[32]

Concn., M.	E.M.F. (volts)	γ obs.	γ calc.
0·025	−0·02051	0·613	0·613
0·05	0·0	0·522	0·535
0·125	+0·02744	0·425	0·432
0·25	0·04809	0·364	0·363
0·5	0·06838	0·308	0·308
1	0·08904	0·263	0·269
1·5	0·10408	0·259	0·253
2·0	0·11432	0·254	0·248

The activity of sulphuric acid in lithium sulphate has been determined using a cell of the type:-

$$\mathrm{H_2} \mid \mathrm{H_2SO_{4(c_1)}}\,\mathrm{Li_2SO_{4(c)}} \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg}.^{32}$$

The equivalent refractivity of lithium sulphate solutions is dependent upon concentration[33] and these results have been used in the evaluation of the degree of dissociation of the salt in fused glass. In comparison with the refractive index of the pure salt and its aqueous solutions at infinite dilution, the values for borax glass are less than expected and the difference is attributed to the strong deformation and meagre dissociation which the salt suffers in the glass medium.[34]

In contrast, the determination of magnetic susceptibility of lithium sulphate in borax glass, using a torsion balance, gives values much larger than those for the pure salt, indicating an expansion of the lattice.[35]

Conductometric methods have also been applied to the determination of the diffusion coefficients of lithium sulphate, and the results given in Tables VII and VIII are in agreement with values calculated from the theory of Fuoss and Onsager.

TABLE VII.-.DIFFUSION COEFFICIENT OF LITHIUM SULPHATE AT 25°C.[36,37]

Concn., M.	Diffusion Coefficient	
	Obs.	Calc.
0·00071	0·997-8	0·998
0·0021	0·973	0·975
0·00348	0·961	0·961
0·0044	0·954	0·955
0·00573	0·946	0·948

The value of the Soret coefficient for lithium sulphate is 1·4 ± 0·1milli-units/°C. and the heats of transference (relative to the chloride ion) calculated from this value are $\mathrm{Li^+} = 0{\cdot}0$, $\mathrm{SO_4''} = 0{\cdot}7$kg.-cal./mol.[39]

TABLE VIII.- DIFFUSION RATE OF LITHIUM SULPHATE[38]

Concn.	Diff. Rate
0·1N.	0·685
1N.	0·626
4N.	0·574

Examination of the lithium sulphate crystal for piezoelectric and elastic properties shows that the salt is piezoelectrically positive[40,41] and, from *X*-ray data over the range –30°C. to +25°C., that thermal expansion is negative in a 45° range roughly normal to *c* in the *a–c* plane. The secondary and total pyroelectric constants of lithium sulphate are 21×10^{-6} and 76×10^{6} coulomb/m.^{2}/°C.[42] The dielectric constant has also been determined as a function of temperature over the range 100–400°K. at 500–20,000c./s. for the crystalline hydrate, and it is concluded that there is little chance of lithium sulphate being ferroelectric below –180°C.[43]

The Raman inactive frequency of lithium sulphate (hydrate) in benzene is 1003·1cm.$^{-1}$, and measurements have also been made on N. and 2N. aqueous solutions.[44]

The thermal stability of lithium sulphate has been studied in comparison with that of sodium and potassium sulphates: the conclusion reached is that a decrease in ionic character of the bond is due to the polarising action of the lithium ions on the anion.[45] The volatility of lithium sulphate as compared with sodium and potassium sulphates is given in Table IX.

TABLE IX.- VOLATILITY OF ALKALI METAL SULPHATE

Temp. °C.	Duration of expt.	Loss in wt.-%		
		Li_2SO_4	Na_2SO_4	K_2SO_4
800		Nil	Nil	Nil
900	2hr.	0·12	Nil	Nil
1000	2hr.	0·51	0·04	0·12
1200	2hr.	1·76%/hr.	0·52%/hr.	1·82%/hr.

The presence of $(Li_3SO_4)^+$ and $(LiSO_4)^-$ in pure molten lithium sulphate is shown by a study of the eutectics of the binary systems Li_2SO_4–$BaSO_4$, Li_2SO_4–$SrSO_4$, Li_2SO_4–$PbSO_4$; by the depression of freezing point of lithium sulphate by small amounts of other metal sulphates; and by the depression of the freezing point of potassium nitrate by small additions of lithium sulphate. Dissociation into Li^+ and $(LiSO_4)^-$ occurs when the concentration of lithium sulphate is moderate, but at low concentrations dissociation yields[46] Li^+ and SO_4^{2-}.

The surface tension of molten lithium sulphate, determined by the maximum bubble pressure method, is:- at 900°C., 224dynes/cm.; at 1100°C., 211dynes/cm.[47]

A photographic study of the diffusion of lithium sulphate in a bunsen flame indicates that at a flame temperature of 1436°C. polymerization of the lithium sulphate is probably responsible for the low rate of diffusion.[48]

Many binary, ternary and quaternary systems involving lithium sulphate have been studied in both aqueous and fused media.

(1) Li_2SO_4–Na_2SO_4–H_2O

When aqueous solutions of sodium sulphate and lithium sulphate are maintained at 27°C. for 24hr. and the solid products in equilibrium with the saturated solution are analysed, three solid phases are found, $Na_2SO_4,10H_2O$, $Na_3Li(SO_4)_2,6H_2O$ and Li_2SO_4,H_2O, while the solution in equilibrium with the solid phase contained Li_2SO_4 5·4%, Na_2SO_4 25·5%, H_2O 69·1%.

Four solid phases (the fourth being $NaLiSO_4$) were reported in a similar experiment carried out at 46·5°C.[49]

The 0°C. isotherm is similar except for the numerical relationships.[50]

(2) $Li_2SO_4-(NH_4)_2SO_4-H_2O$

This system exhibits two ternary eutectics:-

(a) $(NH_4)_2SO_4-(NH_4)_2SO_4,Li_2SO_4$-Ice at −27°C.
(b) $Li_2SO_4-(NH_4)_2SO_4,Li_2SO_4$-Ice at −30°C.

The heat of formation of the double salt is 1·28 ± 0·01kg.-cal.[51]

(3) $Li_2SO_4-M^{++}SO_4$

Double salts of the type:-

$$Li_2SO_4,M^{++}SO_4 \text{ and } 2Li_2SO_4,M^{++}SO_4$$

are formed from zinc, copper, magnesium, cobalt, nickel and vanadium sulphates, although silver sulphate forms only one double salt, Ag_2SO_4,Li_2SO_4.[52] Cadmium sulphate, however, does not appear to form a double salt,[53] and the existence between 0° and 35°C. of the copper sulphate double salt is also questioned.[54]

(4) $Li_2SO_4-M^{3+}{}_2(SO_4)_3$

Bismuth sulphate forms two double salts, viz:-

$$3Li_2SO_4,Bi_2(SO_4)_3,4H_2O$$
$$Bi_2O_3,SO_3,LiSO_4,2H_2O$$[55]

Early attempts to prepare lithium alum proved unsuccessful,[56,57] but a double salt incongruently soluble at 0°C. has recently been obtained.[58]

(5) $Li_2SO_4-K_2SO_4$

Li_2SO_4,K_2SO_4 is formed at 25°C. as the solid separating from solutions containing the two salts, but is considered as only a borderline case of a series of solid solutions which are formed of composition mLi_2SO_4,nK_2SO_4 giving K:Li limits varying from 1:1 to 1:1·08.[59] The crystal structure of $LiKSO_4$ consists of a system of SO_4'' ions in hexagonal close packing alternating with metallic ions.[60]

The equilibrium curves for solutions of the double sulphates of lithium, sodium and potassium with aqueous sulphuric acid have also been studied[61] as has also the four component system $Li_2SO_4-(NH_4)_2SO_4-H_2SO_4-H_2O$.[62]

Binary, ternary and quaternary systems in the molten state have been studied, and many reported eutectics incorporating lithium sulphate are summarised in Table X.

The existence of a eutectic between potassium sulphate and lithium sulphate has also been confirmed by specific conductivity measurements between 266°C. and 1068°C. The conductivity/temperature relationship is then

$$\log K = a + bT$$

where a and b are constants and K is the specific conductivity.[75] The double salts of sodium and potassium sulphates with lithium sulphate have differing hexagonal structures, but though no solid solutions appear to exist between them,[76] the decomposition and other changes occurring during cooling suggest that sodium sulphate does form such a solution.[77]

In an extension of the binary systems of sodium and potassium sulphates with lithium sulphate to the ternary system with potassium nitrate, the phase diagram has five regions where the solid phases and the percentages of the total area they represent are respectively;- K_2SO_4 43·2%; Li_2SO_4 42·7%; Li_2SO_4,K_2SO_4 12%; KNO_3 0·8%; $LiNO_3$ 1·3%.

There are three invariant points:-

(1) A transition point at 440°C. containing 53·5 (equiv.) % SO_4, 58% Li.
(2) A transition point at 133°C. containing 1% SO_4, 43·5% Li.
(3) A eutectic at 103°C. containing 1·0% SO_4, 41·5% Li.[78]

TABLE X.- EUTECTICS CONTAINING LITHIUM SULPHATE

System	Eutectic Temp. °C.	Eutectic Composition Mol.-%		Ref.
Li_2SO_4-Li_2Cl_2	478	53	Li_2SO_4	63
Li_2SO_4-Li_2Cl_2	480	52•5	Li_2SO_4	64
Li_2SO_4-K_2Cl_2	453	68•0	Li_2SO_4	65
Li_2SO_4-Na_2Cl_2	496	87•2	Li_2SO_4	65
Li_2SO_4-K_2SO_4	716	32	Li_2SO_4	65
Li_2SO_4-$CaSO_4$	706	83•8	Li_2SO_4	64
Li_2SO_4-$CaSO_4$	695	83•5	Li_2SO_4	66
Li_2SO_4-$CaCl_2$	627	13•5	Li_2SO_4	64
Li_2SO_4-$CaCl_2$	600	87•5	Li_2SO_4	64
Li_2SO_4-$CoSO_4$	590	72•5	Li_2SO_4	63
Li_2SO_4-$CoCl_2$	548	65	Li_2SO_4	63
Li_2SO_4-$CdSO_4$	550	68	Li_2SO_4	67
Li_2SO_4-$BaTiO_3$	849	99•6	Li_2SO_4	68
Li_2SO_4-$PbWO_4$	754	94•5	Li_2SO_4	69
Li_2SO_4-Li_2WO_4	630			69
Li_2SO_4-Li_2WO_4	854			
Li_2SO_4-Li_2MoO_4	564	62•5	Li_2SO_4	70
Li_2SO_4-Na_2Cl_2-K_2Cl_2	426	24	K_2Cl_2	71
		17	Na_2Cl_2	
		59	Li_2SO_4	
Li_2SO_4-Na_2SO_4-K_2SO_4	512	79	Li_2SO_4	72
		9	Na_2SO_4	
		12	K_2SO_4	
Li_2SO_4-Li_2Cl_2-Li_2WO_4	444	47	Li_2Cl_2	73
		21	Li_2WO_4	
		32	Li_2SO_4	
Li_2SO_4-$CdCl_2$-$CdSO_4$	512			67
Li_2SO_4-Li_2Cl_2-$ZnCl_2$	285	0•5	Li_2SO_4	74
		13	Li_2Cl_2	
		86•5	$ZnCl_2$	
Li_2SO_4-$ZnCl_2$-$ZnSO_4$	293	0•7	Li_2SO_4	74
		90•3	$ZnCl_2$	
		9•0	$ZnSO_4$	

The reaction between lithium chloride and zinc sulphate is irreversible,

$$Li_2Cl_2 + ZnSO_4 \rightarrow Li_2SO_4 + ZnCl_2,$$

two binary compounds occurring:-

(*a*) $Li_2Cl_2,ZnCl_2$ (incongruent m.p. 352°C.)
(*b*) $ZnCl_2,ZnSO_4$ (incongruent m.p. 437°C.)

Eight fields of crystallization of the solid phases were established in the system Li,Zn || Cl,SO_4 corresponding to α- and β-Li_2SO_4, α- and β-LiCl, $ZnCl_2$, $ZnSO_4$, and the compounds (*a*) and (*b*). The system exhibits two ternary eutectic points:-

(1) at 285°C. - Li_2Cl_2 13, Li_2SO_4 0•5 $ZnCl_2$ 86•5mol.%
(2) at 293°C. - Li_2SO_4 0•7 $ZnCl_2$ 90•3 $ZnSO_4$ 9mol.%

and two transition points at 330°C. and 397°C.[74]

When cadmium sulphate replaces the zinc sulphate of the former system, an irreversible reaction occurs:-

$$CdSO_4 + Li_2Cl_2 \rightarrow Li_2SO_4 + CdCl_2 \ (\Delta H = 7{\cdot}99\text{kg.-cal./equiv.})$$

involving three eutectics:-

(a) $CdCl_2$-$CdSO_4$ m.p. 542°C. 15% $CdSO_4$
(b) Li_2SO_4-$CdSO_4$ m.p. 550°C. 32% $CdSO_4$
(c) Li_2Cl_2-Li_2SO_4 m.p. 478°C. 53% Li_2SO_4,

while $CdCl_2$-Li_2Cl_2 exhibits continuous solid solutions, with a minimum at 500°C., containing 77–78% $CdCl_2$ (d).

The four salts are represented at opposite corners of a square phase diagram, and the only stable cross-section consists of a diagonal joining cadmium chloride and lithium sulphate with a eutectic at 543°C. containing 3·5% Li_2SO_4. This divides the square into two ternary systems, $CdCl_2$-Li_2SO_4-Li_2Cl_2 containing the solid solutions Li_2Cl_2-$CdCl_2$ and the field of crystallization of Li_2SO_4; and $CdCl_2$-Li_2SO_4-$CdSO_4$, with a ternary eutectic, m.p. 512°C. The immiscibility is attributed to the different electronic structures of the cations.[67]

In the three dimensional diagram of the Li_2SO_4-K_2SO_4-K_2WO_4 system, the two sections representing varying proportions of Li_2WO_4,K_2WO_4 to Li_2SO_4, K_2SO_4, and Li_2WO_4 to Li_2SO_4,K_2SO_4 are stable, and all other sections metastable. Reactions in the system therefore tend towards the formation of Li_2SO_4,K_2SO_4 and Li_2WO_4,K_2WO_4. The system exhibits three eutectics:- (*a*) at 480°C. Li_2WO_4 20%; K_2SO_4 20%; Li_2SO_4 60%; (*b*) at 484°C. Li_2WO_4 30%; K_2WO_4 37·5%; Li_2SO_4 32·5%; (*c*) at 486°C. Li_2WO_4 47·0%; K_2SO_4 37·5%; K_2WO_4 15·5%; and a transition point at 526°C.[79]

Other systems investigated include:-

(*a*) the ternary system Li || Cl, SO_4, WO_4 eutectic m.p. 444°C. 32% Li_2SO_4, 47% Li_2Cl_2, 21% Li_2WO_4[73]
(*b*) the ternary system Li, Na, Ca || SO_4[77]
(*c*) the reciprocal system Li, K || SO_4, PO_3[80]
(*d*) the ternary system Li, Na || NO_3, SO_4[81]
(*e*) the ternary system Li, K || SO_4, BO_2[82]
(*f*) the ternary system Li, K || MoO_4,SO_4[70]
(*g*) the quaternary system Li, Na, K || SO_4, Cl[71]
(*h*) the quaternary system Li, Na, K, Tl || SO_4[83]
(*i*) the quaternary system Li, K || Cl, SO_4, WO_4[84]

In the estimation of lithium sulphate by precipitation as barium sulphate, the precipitate is liable to be contaminated by coprecipitation of lithium sulphate. Solid solutions of substitutional type are formed containing $BaSO_4$, Li_2SO_4 and water, for low concentrations of Li^+. For precipitates of higher lithium concentration, solid solutions of $BaSO_4$, $LiHSO_4$, Li_2SO_4 and water are indicated which contain one mol. of water per Li^+, retained after extensive drying at 110°C.[85] A suitable analytical procedure has been developed for the estimation of lithium sulphate by precipitation as barium sulphate.[86]

Lithium sulphate has been employed in the preparation of hydrogen peroxide[87] and persulphates[88] by electrolysis, and the oxygen overpotential in the fused melts of lithium sulphate in lithium sodium fluoride has also been studied.[89]

Lithium sulphate also finds application in the preparation of catalysts for the dehydrogenation of *cyclo*hexanol and *cyclo*hexanone to phenol[90] and in the preparation of casting material in conjunction with gypsum.[91]

Lithium sulphate solutions containing acidified ferrous sulphate are oxidized by thermal neutrons and the neutron dose may thus be followed from the course of oxidation of the iron.[92]

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SECTION XVI

LITHIUM CARBONATE

By R. E. OLIVER

Preparation and Production

Lithium carbonate may be prepared in the laboratory by the following methods.

(*i*) The double decomposition of a solution of a lithium salt with a solution of an alkali metal carbonate. Probably the most frequently used reaction of this type is that between lithium sulphate and sodium carbonate, $Li_2SO_4 + Na_2CO_3 \rightarrow Li_2CO_3 + Na_2SO_4$.

Owing to the appreciable solubility of lithium carbonate in solutions of other salts, a recovery of only about 75% can be achieved. Lithium carbonate prepared in this way is contaminated with small quantities of both sodium and sulphate. Ammonium carbonate may be used as precipitating agent, when a purer product is obtained but in poor yield.

(*ii*) The action of carbon dioxide on lithium hydroxide, $2LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O$.

As both reactants are obtainable in a high state of purity, lithium carbonate of very high quality may be prepared by this method.

Lithium carbonate may be purified by utilizing its reverse solubility in water.[1] The small difference in solubility (1·5% approximately at 20°C, and 0·8% approximately at 100°C.) makes the method difficult to apply on anything but a small scale. A reprecipitated lithium carbonate of high quality is obtained. The salt may also be purified by treating an aqueous suspension with carbon dioxide either under pressure or at reduced temperature. A solution of lithium bicarbonate is formed which is decomposed again to carbonate on boiling.

In recent years the greatly increasing interest in lithium compounds has resulted in the development of several new processes for the extraction of lithium as lithium carbonate. In a process used in America[2] crushed spodumene (a lithium aluminium silicate containing approximately 3-5% Li_2O) is heated to 1100°C. in a rotary kiln. At this temperature the change in structure to β-spodumene is almost instantaneous and is accompanied by a breakdown to a form which can be readily milled to a fine powder. The finely milled ore is mixed with concentrated sulphuric acid and heated to 250°C. In this way lithium is replaced by hydrogen in the structure and may be almost quantitatively extracted as lithium sulphate by leaching with water. The leach solution is purified by precipitating magnesium with calcium hydroxide, removing excess calcium with sodium carbonate, and then adding sulphuric acid to pH 7 when iron and aluminium are precipitated by boiling. The pure lithium sulphate solution is then concentrated and lithium carbonate is precipitated with sodium carbonate, washed with water and dried. A yield of approximately 80% and a purity of 98% is claimed. This process is equally applicable to petalite, a lithium aluminium silicate similar to spodumene, found abundantly in Rhodesia.

Two processes,[3,4] similar in detail and designed to extract lithium from amblygonite (lithium aluminium fluoro-phosphate) and from lepidolite (lithium mica) have been patented. The minerals are heated with potassium sulphate or bisulphate and leached with water. A solution containing essentially lithium sulphate and potassium sulphate is obtained by removing elements such as iron, aluminium, calcium and magnesium in a manner similar to that described above. Direct precipitation of this solution gives a recovery of lithium carbonate of 30–60%. The addition of potassium chloride to the solution salts out potassium sulphate, giving a solution of potassium and lithium chloride in which sulphates are relatively insoluble. Lithium carbonate is then precipitated with potassium carbonate. The filtrate, essentially potassium chloride containing dissolved lithium carbonate is reused for the precipitation of subsequent batches of potassium sulphate. A recovery nearly theoretical and a purity of approximately 99% are claimed.

Physical Properties

Spectra.

Lithium carbonate shows strong characteristic absorption bands at the following frequencies:- 1096, 870, 860, 741, 740 and 711 cm.[1,36]

Density.

The accepted figure for the relative density is 2·111. The apparent bulk density of the material is approximately 40lbs./cu.ft. This figure may vary substantially with different methods of formation or precipitation.

Solubility.

The solubility in water has been determined by Haehnel,[5] with the results given in Table I.

TABLE I. - SOLUBILITY OF LITHIUM CARBONATE IN WATER

Temp. °C.	Parts Li_2CO_3/100 parts water
0	1·539
20	1·329
50	1·181
100	0·720

The solubility and solubility product of lithium carbonate are considerably affected by common ions.[6] Addition of lithium chloride has little effect on the solubility product but the solubility falls sharply, while the addition of sodium carbonate has very little effect on the solubility but causes a sharp increase in the solubility product. Both the solubility and the solubility product show the reverse behaviour with respect to temperature that is usual with lithium salts.

Aqueous Systems containing Lithium Carbonate.

The solubility isotherms of the systems Li_2CO_3-Na_2CO_3-H_2O and Li_2CO_3-K_2CO_3-H_2O have been determined at 25°C.[7,8] The isotherm of the first system has two branches, of Li_2CO_3 and of $Na_2CO_3,10H_2O$; similarly the second has two branches, of Li_2CO_3 and of $K_2CO_3,2H_2O$. Contrary to the findings of Lagarde,[6] the effect of the common ion on the repression of combined solubility was found to be normal. No evidence of solid solutions or double salts was found.

Fused Systems containing Lithium Carbonate.

Li || Cl, CO_3, SO_4.

This ternary system has been studied by a visual polythermal method.[9] The liquidus diagram of the system has three fields of crystallisation of the components. The ternary eutectic point is 455°C. with a composition of LiCl 36 mole % and Li_2CO_3 27 mole %. The eutectic of the system Li || Cl, CO_3 was 507°C. with 61 mole % LiCl.

Li, Na || SO_4, CO_3.

The liquidus surface of this system contains[10] a crystallization field of continuous solution of Na_2CO_3 and Na_2SO_4, fields of Li_2SO_4 and Li_2CO_3 and of the compounds $Li_2SO_4,2Na_2SO_4$, Li_2SO_4,Na_2SO_4 and Li_2CO_3,Na_2CO_3. The system has two triple eutectic points.

Li, Rb || F, CO_3.

The liquidus surface of this system consists[11] of the crystallisation fields of the components and the compounds RbF,Rb_2CO_3 and Rb_2CO_3,Li_2CO_3.

The Action of Heat on Lithium Carbonate.

The melting point of lithium carbonate is now reported as 723°C.[12]

The thermal dissociation has been studied using a gold platinum alloy reaction vessel in conjunction with a manometer system,[13] and the results are given in Table II.

TABLE II. - DISSOCIATION PRESSURES OF LITHIUM CARBONATE

Temp. °C.	pCO_2 (mm.Hg)
750	0
800	3·1
850	8·1
900	17·4
950	32·7
1000	56·2
1100	134·4

Above 1100°C. appreciable volatilisation of lithium carbonate occurs. Differential thermal studies show[14] that decomposition begins at approximately 700°C. and is complete at 1310°C. No great accuracy was claimed for these figures owing to difficulties arising from poor thermal diffusion in the apparatus employed. More recently,[12] however, there has been confirmation of the view that decomposition begins at a temperature below 750°C. Using a sample containing 1% of impurity, differential thermal analysis indicated that decomposition commenced at 708°C. Lithium carbonate heated to 950°C. still contained 6.19% CO_2.

Surface Tension.

It has been postulated[15] that if a salt increases the surface tension of water it decreases the solubility of a non-conductor dissolved in the salt solution, and that the reverse is also true. This is verified by the fact that lithium carbonate reduces the solubilities of glycerol, acetone, acetamide, methyl alcohol, acetonitrile and urethane in aqueous solution.

Diffusion.

The diffusion of lithium carbonate in water has been studied by Öholm.[16] Because of its large water envelope the lithium ion has a small diffusion coefficient, following the series:-

$$K^{\cdot} > Na^{\cdot} > Li^{\cdot}$$

Magnetic Susceptibility.

Recent determinations[17] using a modified form of Guoy's balance give the value $-29{\cdot}3 \times 10^{10}$ e.s.u.

Chemical Properties

The general reactions of lithium carbonate to form other lithium salts are well known. The behaviour of this salt in reactions more recently studied is summarised below.

Lithium carbonate dissociates when heated according to the equation:-

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

The reaction is reported to commence at 708°C.[12] and to be complete at 1310°C.[14] At this temperature lithium carbonate itself is appreciably volatile. If carbon dioxide is continuously removed the conversion to lithium oxide may be readily and completely effected at 1000°C.[18]

Lithium carbonate reacts with carbon dioxide and water to give a bicarbonate solution:-

$$Li_2CO_3 + CO_2 + H_2O \rightarrow 2LiHCO_3$$

The equilibrium constant, K, for the formation of bicarbonate has been determined at 0°C. and 16•5°C.,[19] as follows:- K_0 0•250, K_{165} 0•192. The reverse nature of these figures is confirmed by the work of Haehnel[5] who showed the maximum solubility of lithium bicarbonate to be 22•71% at -12°C. under a pressure of 5 atm. of carbon dioxide. Dilute solutions are stable at atmospheric temperature and pressure. The solubility falls progressively with rise in temperature so that at 60°C. a pressure of 50 atm. of carbon dioxide is required to maintain the maximum solubility of 9•61%.

Lithium bicarbonate exists only in solution, lithium carbonate being reformed when the solution is decomposed by heat. The heat of formation in solution from lithium carbonate and carbon dioxide is 1350g.-cal./mol. The heat of solution is 2180g.-cal./mol.[20]

A stable form of lithium bicarbonate is reported to have been isolated,[21] a precipitate stable at 30°C. having been prepared from a solution of lithium bicarbonate containing gelatin by adding alcohol.

The equilibrium between solutions of lithium carbonate at 25°C. and air containing 300–350p.p.m. of carbon dioxide has been studied.[22] The activity coefficients for HCO_3^- (α) and CO_3^{--}(β) given in Table III are determined on the assumption that

$$\frac{d \log \beta}{d \log \alpha} = 4$$

a postulate of the Debye–Hückel theory valid at ionic strengths approaching zero.

TABLE III. - ACTIVITY COEFFICIENTS FOR LITHIUM CARBONATE AND BICARBONATE

Molality	α	β
0	1•000	1•000
0•01	0•896	0•646
0•02	0•862	0•552
0•04	0•819	0•451
0•06	0•790	0•389
0•08	0•767	0•345
0•10	0•747	0•312
0•20	0•683	0•218

Lithium carbonate is decomposed very slowly by boiling water to form the hydroxide.[23] If carbon dioxide is continuously removed from the atmosphere above the solution, it is found that 71% of a 0•27 N. solution decomposes in 10 days.

Lithium carbonate solutions are also hydrolysed to a small extent at room temperature. A four stage mechanism covering the range 0•1 N. to less than 0•0001 N. has been postulated.[24] A solution containing 0·102 moles/l. was progressively diluted to twice its volume with redistilled water, with the following results:-

(*i*) Concentration approximately 0•1 N.

pH (per dilution) 0·05
$(CO_3^{--})_3 + 3H_2O \rightleftharpoons 3CO_3H^- + 3OH^-$
Hydrolysis constant Li $4{\cdot}8 \times 10^{-16}$
Percentage hydrolysis 1–5%.

(ii) Concentration approximately 0·01 N.
pH (per dilution) 0·2
$2CO_3^{--} + 2H_2O \rightleftharpoons (CO_3H^-)_2 + 2OH^-$
Hydrolysis constant Li $1{\cdot}58 \times 10^{-6}$
Percentage hydrolysis 5–12%.

(iii) Concentration approximately 0·001 N.
pH (per dilution) 0·9
$CO_3^{--} + 5Li^+ + H_2C \rightleftharpoons (CC_3Li_5H)^{4+} + OH^-$
Hydrolysis constant Li 8×10^{-8}
Percentage hydrolysis decreases from 12 to 0·2%.

(iv) Concentration approximately 0·0001 N.
pH (per dilution) 0·15
$CO_3^{--} + H_2C \rightleftharpoons CO_3H^- + OH^-$
Hydrolysis constant 4×10^{-10}
Percentage hydrolysis 0·2 to 0·5%.

In many cases lithium carbonate in solid reactions at elevated temperature provides a source of lithium oxide. Its subsequent behaviour is considered under the reactions of lithium oxide.

An equimolecular mixture of lithium carbonate and gallium oxide heated for 4 hr. at 900°C. in an atmosphere of dry hydrogen sulphide[25] and cooled under hydrogen sulphide gives as the product $LiGaS_2$. This compound exists in a light brown rhombic crystalline fom, ρ 2·98, m.p. 1020 ± 5°C., and is stable to boiling water.

The action of carbon on lithium carbonate gives carbon monoxide and a lithium carbide of the composition Li_2C_X, which is thought to be lithium carbide dissolved in lithium.[26]

The action of chlorine on lithium carbonate[27] yields lithium chloride at temperatures above 350°C. The reaction proceeds much less readily than with sodium or potassium carbonate and, in contrast to these elements, no perchlorate is formed.

Nascent chlorous acid, prepared by dissolving chlorine dioxide in water, reacts with lithium carbonate solution to give lithium chlorite.[28] A solution of the acid, lithium carbonate and twice the stoicheiometric quantity of hydrogen peroxide is allowed to stand for 5 hr. at 2°C. Lithium chlorate is also formed.

Applications and Uses

The major part of the lithium carbonate produced finds application in the ceramic industry. Many of the properties of ceramic glazes and enamels may be altered advantageously by the addition of small quantities (usually in the range 0–5%) of lithium carbonate to the frits from which they are prepared. These advantageous modifications include the lowering of the temperature of vitrification,[29] of the temperature of softening, and of the coefficient of thermal expansion, and improving the gloss and the wetting characteristics of the molten glaze.[30]

A minor ceramic application is found in the production of dielectric materials. Bodies with very low dielectric loss factors are prepared by adding very small quantities of lithium carbonate to the standard materials.[31]

Lithium carbonate has been found to give satisfactory results as a catalyst in the decomposition of hydrocarbon oils with steam. A mixture of oil and steam passed through the catalyst bed is converted to a combustible gas containing large quantities of methane, hydrogen and carbon monoxide.[32]

A further small application of lithium carbonate is in the preparation of phosphors, in which increased luminescence may be achieved by activation with small quantities of lithium carbonate. Phosphors based on strontium sulphide, strontium hydroxide and calcium carbonate are specifically mentioned.[33,34]

Cements with relatively high alkali content when mixed with rock aggregate to form concrete, react and expand. In the course of time this reaction leads to a deterioration in the concrete strength owing to cracking. Lithium carbonate has been found to be most effective in reducing this expansion, when added in the proportion of 1% of the cement.[35]

Analytical

The possible use of lithium carbonate as a flux in spectrochemical analysis has been proposed,[37] the sample, diluted nine times with lithium carbonate, being burned to completion between graphite electrodes. High accuracy has not so far been achieved.

In determining the isotopic composition of lithium, samples of lithium carbonate of unknown isotopic composition and a standard sample are placed on a photographic plate and irradiated with neutrons.[38] After development the plate is evaluated photometrically.

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SECTION XVII

LITHIUM NITRATE

By G. SCHOLES

The crystal structure of lithium nitrate has been examined by X-ray methods[1] and found to have the following parameters: $r = 5{\cdot}74 \pm 0{\cdot}02$ A, $\alpha = 48°3' \pm 10'$, $d = 2{\cdot}38$, $u = 0{\cdot}264 \pm 0{\cdot}006$. The crystals are isomorphous with sodium nitrate.

Lithium nitrate melts[2] at 251•4°. Davis, Rogers and Ubbelohde have suggested[3] that the low melting points of Group I nitrates, as compared with those of the corresponding halides, are due to the formation of association complexes in the nitrate melts. From a survey of published data on the electrical conductances and viscosities of lithium nitrate melts, these authors have derived values of the activation energies for ionic conductance (E_σ) and for viscous flow (E_η), using the relationships:

$$\ln\sigma = \sigma_0 - \frac{E_\sigma}{RT} \text{ and } \ln\eta = \eta_0 - \frac{E_\eta}{RT}$$

Table I shows the values obtained over various temperature ranges.

TABLE I.- ACTIVATION ENERGIES FOR IONIC CONDUCTANCE (E_σ) AND FOR VISCOUS FLOW (E_η) IN LITHIUM NITRATE MELTS

Temp. range (°C.)	E_σ (kg.-cal./mol.)	σ_0	Temp. range (°C.)	E_η (kg.-cal./mol.)	$10^4\eta_0$
270–290	4•49	55•4	260–354	4•23	11•90
400–440	2•83	3•3	354–429	6•91	1•38

The coefficient of internal fraction of the fused salt (η') has been measured at different temperatures over the range 260° to 429°.[4] The experimental results fall on a curve which can be represented by the equation $\eta' = A + Bt + Ct^2 + Dt^3$, where t is the temperature, $A = 0{\cdot}31896$, $B = -1{\cdot}754 \times 10^{-3}$, $C = 3{\cdot}831 \times 10^{6}$ and $D = -3{\cdot}23 \times 10^{9}$.

Compound formation involving lithium nitrate has been observed in only a few systems and the relevant information is recorded in Table II.

TABLE II.- MOLECULAR COMPOUNDS CONTAINING LITHIUM NITRATE

System	Compound formed	Reference
$LiNO_3$–$RbNO_3$	$LiNO_3, RbNO_3$ m.p. 191°	5, 6
$LiNO_3$–$LiOH$	$LiNO_3, LiOH$ decomposes at 195°	7
$LiNO_3$–$CO(NH_2)_2$	$LiNO_3, 2CO(NH_2)_2$ m.p. 126°	8

Several other binary and ternary systems containing lithium nitrate have been investigated; data are available for the following:

	Reference
$LiNO_3$–$Cd(NO_3)_2$–$NaNO_3$	9

	Reference
$LiNO_3$-$Cd(NO_3)_2$-KNO_3	9
$LiNO_3$-$Cd(NO_3)_2$	9,10
$LiNO_3$-NH_4NO_3	11,12
$LiNO_3$-NH_4NO_3-guanidine nitrate	13
$LiNO_3$-hydrazine nitrate	14
$LiNO_3$-$AgNO_3$-NH_4NO_3	15
$LiNO_3$-acetic acid	16
$LiNO_3$-$NaNO_3$-$Ca(NO_3)_2$	17
$LiNO_3$-$Ca(NO_3)_2$	18
$LiNO_3$-KNO_3-$Ca(NO_3)_2$	19
$LiNO_3$-$AgNO_3$	20
$LiNO_3$-$TlNO_3$	21,22
$LiNO_3$-KNO_3-$TlNO_3$	22
$LiNO_3$-K_2SO_4-KNO_3	22
$LiNO_3$-$Sr(NO_3)_2$	23
$LiNO_3$-$NaNO_2$-KNO_2	24
$LiNO_3$-$Pb(NO_3)_2$-H_2O	25,26
$LiNO_3$-NH_4NO_3-H_2O	11

Some thermochemical data for lithium nitrate, in the solid state as well as in solution, have been reviewed by Bichowsky and Rossini.[27] The heat of formation of the salt from its elements is given as 115·352kg.-cal. and the heat of solution in water S_{200} = 0·333kg.-cal.

The transition of the trihydrate, attributed to the reaction $LiNO_3,3H_2O \rightarrow LiNO_3,\frac{1}{2}H_2O + 2\frac{1}{2}H_2O$, (Mellor, II, 815) has been studied in alcohol[28] and also in pyridine, acetone and amyl alcohol.[29] The transition point, calculated from electrolytic resistance-temperature data, was found to be independent of the nature of the solvent and, within the accuracy of the experiments, the same as the value found in water (29·6°). Some doubt has been cast on the existence of the hemihydrate.[11] In the system $LiNO_3$-NH_4NO_3-H_2O this particular hydrate does not appear to exist as a stable solid phase. A direct investigation of the transition point in the $LiNO_3$-H_2O system, using the dilatometer technique, failed to reveal the transition $LiNO_3,\frac{1}{2}H_2O \rightarrow LiNO_3 + \frac{1}{2}H_2O$, which is said to occur at 61·1°.

The solubility of lithium nitrate in several organic solvents has been determined[30] with results given in Table III. It has been shown[31] that lithium nitrate is much less soluble in hydrogen peroxide than in water; definite discontinuities in the curve for mole fraction of hydrogen peroxide in the solvent versus molality of the salt indicate the appearance of new solid solvate phases separating from the water-rich solvents.

TABLE III.- SOLUBILITY OF LITHIUM NITRATE IN ORGANIC SOLVENTS

Solvent	Solubility (g./100c.c. solvent) At 0°	At 25°
iso Amyl alcohol	5·41	9·5
Acetonitrile	-	2·99
Pyridine	27·4	37·15

The vapour pressures of aqueous solutions at 25° have been determined over a wide concentration range, from 0·1N. to saturation.[32,33] Vapour pressure data have been used for the calculation of the chemical potential of lithium nitrate in aqueous solution[34] and also to obtain values for the mean activity and osmotic coefficients of the ions.[33,35] The results are given in Table IV.

The diffusion coefficients of fairly concentrated aqueous lithium nitrate solutions, given in Table V, indicate that ion-pair formation occurs to only a small extent.[36]

TABLE IV.- ACTIVITY AND OSMOTIC COEFFICIENTS OF LITHIUM NITRATE IN AQUEOUS SOLUTION[35]

Concentration (Molar)	Activity coefficient γ	Osmotic coefficient ϕ
0·1	0·788	0·938
0·5	0·726	0·954
1·0	0·743	0·997
2·5	0·896	1·134
5·0	1·310	1·352
10·0	2·455	1·637
13·5	3·398	1·754

TABLE V.- DIFFUSION COEFFICIENTS OF AQUEOUS LITHIUM NITRATE SOLUTIONS AT 25°

Concentration (Molar)	Diffusion coefficient (cm.^{2} sec.$^{-1}$ × 10^{-5})
0·1	1·240
0·5	1·260
1·0	1·293
2·5	1·336
5·0	1·238

The electrical conductivities of solutions of lithium nitrate in various solvents have been investigated. With 0·0001 to 0·002N. solutions in pure ethanol, the decrease in conductivity is proportional to the square root of the equivalent concentration.[37] Conductivity and also viscosity measurements have been carried out in several binary alcoholic systems, at 25°, using lithium nitrate concentrations varying from 0·1 to 0·00625M.[38,39] These particular systems were as follows: methanol-water, methanol-ethanol, ethanol-water, *n*-propyl alcohol-water, *iso*propyl alcohol-water, ethanol-*n*-propyl alcohol, ethanol-*iso*propyl alcohol and *n*-propyl alcohol-*iso*propyl alcohol. In all systems containing water a maximum was found in the viscosity-composition curve. Only one system, viz. methanol-water, exhibited a minimum in the conductivity-composition curve. In solvents containing only alcohols no maxima or minima were observed in either the viscosity or conductivity-composition curves.

Klochko and Grigor'ev[40,41] have compared the conductivities and viscosities of solutions of lithium nitrate in water at various temperatures with the corresponding properties of solutions of the salt in methanol. It was found that, generally, the property curves of lithium nitrate in methanol resembled closely the analogous curves in water, except for the numerical values. At 25°, the conductivity maximum in water coincided with 10·3mol.-% of lithium nitrate and in methanol with 8·2mol.-%. The absolute values of the conductivities at 25° and at 50° in water were 5·8 to 5·9 times the corresponding values in methanol, whereas the viscosities in methanol were only 1·34 to 0·35 times the corresponding values in water. Apparently, the interaction of the components in the two systems is quite different. Table VI gives some data[42] for the conductivity and viscosity, at 25°, for comparative concentration of $LiNO_3$ in water, in methanol and in water-dioxan (1:1). Qualitatively, the decrease in conductivity on going from water to dioxan-water mixtures can be explained by a decrease in the dielectric constants and a decrease in the dipole moments of the three solvents.

TABLE VI.- ELECTRICAL CONDUCTIVITY AND VISCOSITY OF SOME SOLUTIONS OF LITHIUM NITRATE IN VARIOUS SOLVENTS

Solvent	Concentration (mol.-%)	Conductivity (ohm^{-1} cm^{-1})	Viscosity (centipoise)
Water	8·91	0·1629	1·487
Methanol	9·09	0·0290	2·067
Dioxan	8·81	0·00485	2·704

Electrokinetic potentials of aqueous lithium nitrate solutions have been determined using concentrations up to 0·01N.[43,44]

Some figures are available[45] for the surface tension of solutions of lithium nitrate (5% to 15%) in water and also in 10%-, 20%- and 30%-acetone/water mixtures at 20° and at 40°.

Lithium nitrate is very soluble in liquid ammonia[46,47] and Table VII gives some values at selected temperatures. The solubility curves indicate the formation of the compounds $LiNO_3,8NH_3$, $LiNO_3,4NH_3$ and $LiNO_3,2NH_3$ in the temperature intervals −81° to −52°, −52° to 8° and −8° to 12·5° respectively. At ordinary temperatures, saturated solutions of the salt in liquid ammonia have moderate vapour pressures[48] (see Table VIII) and this has aroused interest in the use of this system in refrigerators.[49-51]

TABLE VII.- THE SOLUBILITY OF LITHIUM NITRATE IN LIQUID AMMONIA

Temp. °C.	Solubility (wt. %)
−77·7	0
−54·0	35·66
−28·5	40·51
5·5	44·28
42·0	71·59
160	82·60
264	100

TABLE VIII.- VAPOUR PRESSURE OF AMMONIA OVER SATURATED SOLUTIONS OF LITHIUM NITRATE IN LIQUID AMMONIA

Temp. °C.	V.p.(mm. Hg)
10	102
20	155
30	230
50	455

Other physicochemical properties of the lithium nitrate-liquid ammonia system which are available[47] include the specific gravity of solutions at 20° and and the electrical conductivity of saturated solutions in the temperature range −33° to 20°. It has also been shown[47] that the decomposition potential of the nitrate in liquid ammonia falls from 5·2V. at −40° to 4·0V. at 25°. The molar heat of the salt in liquid ammonia at −33·4° is 10·8kg.-cal.[52]

Lithium nitrate dissociates above its melting point according to the equation $2LiNO_3 \rightleftharpoons 2LiNO_2 + O_2$, the reaction being reversible. Under conditions of standard pressure it has been found[53] that the temperature of dissociation is 474·1°. From determinations of the temperatures of dissociation at a series of pressures the heat of dissociation has been calculated as −25·09kg.-cal.[54]

The products of the reduction of lithium nitrate trihydrate, $LiNO_3,3H_2O$, by hydrogen in a silent discharge are lithium hydroxide, lithium nitrite, ammonia and nitrogen dioxide.[55] Photochemical reduction of the anhydrous salt to nitrite and oxygen by light from a high pressure mercury arc has a quantum yield of approximately 0·002 and the rate of photolysis is little affected by temperature in the range 30°–200°.[56]

Lithium nitrate reacts with monosodium dioxide, NaO_2, in liquid ammonia to form solid products containing fairly large proportions of lithium peroxide. The nitrate does not react with monopotassium dioxide under these conditions.[57]

When solutions of lithium nitrate in acetone are passed through an ion-exchange column (Dowex A1) the salt is highly absorbed.[58] This absorption is not an ionic exchange and it has been suggested that it is due to the presence, in the absorbed state, of the complex $[Li(NO_3)_2]^-$.

The etching effect of molten lithium nitrate on glass has been examined.[59] It is found that glasses treated in this manner readily break and that the method cannot be used in practice. It seems that the glass undergoes a chemical change; the sodium in it is replaced by lithium, the structure is loosened and the expansion coefficient is thus changed.

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SECTION XVIII

LITHIUM PHOSPHATE

By L. PRATT

The ternary system $Li_2O-P_2O_5-H_2O$ has been studied at 0°C. and 20°C.;[1,2,3] the dilithium salt Li_2HPO_4 was not formed under the conditions studied. Neither Li_3PO_4 or LiH_2PO_4 is hydrated. The neutral phosphate, Li_3PO_4, cannot be prepared in a pure state either by exact neutralisation of orthophosphoric acid by lithium hydroxide or by metathesis between an alkali phosphate and a neutral lithium salt.[5] The neutralisation method gives a precipitate having the composition of a hemihydrate, $Li_3PO_4,0{\cdot}5H_2O$, and since the water is removed only at red heat it is possible that the compound is really the salt $Li_6H_2P_2O_9$ of the acid $H_8P_2O_9$. Complete neutralisation of orthophosphoric acid by lithium hydroxide at 100°C. is said to give lithium hydroxyapatite, $3Li_3PO_4,LiOH$.[5] The neutral phosphate is produced together with phosphine, when lithium hydroxide is heated with red phosphorus.[6] The dihydrate, $Li_3PO_4,2H_2O$, is produced if the salt prepared by adding phosphoric acid to an excess of lithium hydroxide solution is dried at about 16°C. The dihydrate is converted to the hemihydrate by drying at 60°C. for several days.[16] The solubility in water of Li_3PO_4 is given as $0{\cdot}022 \pm 0{\cdot}001\%$ at 0°C. and $0{\cdot}03 \pm 0{\cdot}002\%$ at 20°C.;[1] the compound is too soluble to be used in the gravimetric determination of lithium.[8] In another attempt to determine the solubility it was found that when the salt was in contact with water at a constant temperature for several days a colloidal suspension was produced which could not be filtered off; however, the specific conductivity of the saturated solution at 25°C. was found to be $9{\cdot}37 \times 10^{-4}$ ohm^{-1}cm.$^{-1}$ (corrected for the conductivity of water) and from this result the solubility at 25°C. was calculated to be 0·297g./l.[16]

The crystallographic unit cell dimensions of Li_3PO_4 are $a = 4{\cdot}86$A., $b = 10{\cdot}26$A., and $c = 6{\cdot}07$A., the lithium ions probably occupying three quarters of the octahedral holes between the close-packed oxygen atoms.[7] This salt has been used as a flux to dissolve contaminating metal oxides during the coating of iron wire with copper-nickel alloys.[9]

The mono- and dilithium phosphates, LiH_2PO_4 and Li_2HPO_4, are said to be produced by acidifying the neutral salt.[10] Monolithium phosphate undergoes thermal dissociation between 160° and 260°C. to give the hydropyrophosphate, $Li_2H_2P_2O_7$, which itself dissociates between 260° and 400°C. to give the metaphosphate, $LiPO_3$. The activation energies for the two dissociations are given as 12 and 15kg.-cal./mole respectively.[11] The dielectric constant of LiH_2PO_4 at 9500mcs./sec. has been measured between 50° and 300°C.,[12] but no discontinuous change corresponding to a phase transition was observed. The monolithium salt has a solubility in water of $55{\cdot}8 \pm 0{\cdot}1\%$ at 0°C.[1]

Lithium salts of polymeric condensed phosphates are less dissociated in solution than those of the other alkali metals.[13] Solid melts of lithium polyphosphates have glass-like properties.[4] A 1% solution of lithium pyrophosphate, $Li_4P_2O_7$, is hydrolysed only slowly to the neutral orthophosphate.[14] Lithium tetraphosphate, $Li_6[P_4O_{13}]$, has not been obtained in a crystalline state although it is known in solution.[15]

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SECTION XIX

THE SPECTROSCOPY OF LITHIUM AND CERTAIN OF ITS COMPOUNDS

By R. F. BARROW and LADY ANNE THORNE

THE SPECTRUM OF ATOMIC LITHIUM

By A. THORNE

Introduction

The spectrum of atomic lithium has been much investigated since the early days of spectroscopy, and indeed the study of the alkali metal spectra played an important part in the development of modern spectroscopic theory. Brief historical accounts with references are given in most of the standard text-books on spectroscopy,[1-3] and some review articles.[16,17]

A description of the lithium spectrum and its explanation in terms of modern theory are to be found in relevant text-books.[1-6] The neutral lithium atom has the ground state electron configuration $1s^2\ 2s\ {}^2S_{1/2}$, and so Li I has a doublet spectrum. The first doublet of the principal series, corresponding to the transition $2s\ {}^2S_{1/2}-2p\ {}^2P_{1/2,3/2}$, is at 6708 A., and the rest of the principal series is in the ultra-violet region. The sharp and diffuse series lie in the visible and near ultra-violet regions, and the fundamental series in the infra-red. The most important energy levels and transitions of Li I are shown diagrammatically by Grotrian.[7] Li II is a helium-like ion with the ground state $1s^2\ {}^1S_0$, and Li III is of course a one-electron hydrogen-like ion. Numerical values of the energy levels of Li I, II, and III found experimentally have been tabulated by Bacher and Goudsmit,[8] and more recently and more comprehensively by the National Bureau of Standards.[9]

The first tabulations of line series were given by Fowler[10] and Paschen and Götze[11] for Li I. Later tables compiled by Moore[12,13] give many multiplets of Li I and II from 13,000 A. to the far ultra-violet, together with a finding list arranged by wave-length. The M.I.T. wave-length tables,[14] which list the arc and spark lines of all elements between 10,000 A. and 2,000 A. in order of wave-length, include a list of the 'raies ultimes'; these are also given in the Vatican Observatory 'Atlas of Persistent Spectra'.[15]

In 1938 Shenstone[16] published a summary of spectroscopic work on the arc and spark spectra of all elements, incorporating tables showing how thoroughly each spectrum had been investigated. Meggers[17] brought the information up to date in 1946. At the same time Hartree[18] presented in a similar way a summary of the valculations on atomic wave-functions, of which a large number have been made on the relatively simple two- and three-electron atoms represented by Li^+ and Li.

Astrophysics.

Lithium spectral lines of astrophysical interest are listed in Moore's multiplet tables.[12,13] The resonance lines 6708 A. have been identified in the solar spectrum,[19-21] where they appear to be less intense in the disc than in spot spectra.[19,20] Compared to other metals, lithium is much scarcer in the sun than on the earth.[21]

The resonance lines of lithium have also been found in absorption in a few stellar spectra.[22-26]

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Excitation

The spectrum of lithium has been excited in flames, arcs, sparks, and various forms of discharge and also observed by several methods in absorption. In this sub-section reference is made only to those papers in which the conditions or mechanism of excitation has been the main consideration. Wavelength and intensity measurements of spectral lines and accounts of specialised sources for particular investigations are described in later sub-sections; in particular, references to various forms of spark source are given in the sub-section on ionised lithium (see page 269).

Flames, Furnaces and Collision Processes.

Many investigations have been made of the relation between the intensity of the spectral lines emitted by lithium atoms in various sorts of flame and the concentration of the lithium salts.[1-5,36] This relation has been generally shown to follow a linear law at low concentrations and a square-root law at higher concentrations. Different methods of introducing the salt into the flame have been described.[1,5,6] The distribution in the flame of the excited atoms,[7,36] the effect of adding salts of other alkalies,[8,9] and photoluminescence in flames[13] have all been studied.

Both emission and absorption spectra have been examined in the electric furnace and in exploding wires.[10-12]

The reversal temperature of the red resonance line of lithium (*i.e.*, the brightness temperature of a continuous background against which it just vanishes) has been used to measure flame temperatures[14] and the advantages and limitations of the method have been discussed.[15]

Lines of the lithium spectrum have been excited by collisions with hydrogen and helium atoms.[16] They have also been identified in the luminous trails of ultraspeed pellets containing lithium.[39]

Arcs.

The emission of lithium lines in arc sources has been studied with reference to their spatial distribution, luminous duration, voltage dependence, etc.[17-20] Reversal with increasing concentration has been noted.[21] The effect of adding varying amounts of other alkalies has been investigated with particular reference to methods of quantitative analysis.[20,22] Running the arc in an atmosphere of argon has been found to favour excitation of the spark spectrum.[38]

Discharges.

The emission of the lithium spectrum from anode rays has been studied in some detail.[23-29] Relative intensities of the alkali metal spectra in discharges passed through amalgams have been measured.[30,31] The Li I and Li II spectra have been studied in the negative glow[32,33] and the Li I spectrum in electrodeless discharges.[34,35] The hollow-cathode discharge has been used as a source in determining the ^{6}Li:^{7}Li abundance ratio by spectroscopic methods.[37]

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The Spectrum of Neutral Lithium

The neutral lithium atom has the ground-state configuration $1s^2\ 2s\ ^2S_{1/2}$, with an ionisation potential of 5·390 V., corresponding to a term value for the ground state of 43,487·19 ± 0·02 cm.$^{-1}$, or a wave-length limit of 2298·814 A. for the principal series.[1]

The results of early work are summarised in Fowler's tables,[4] which include the first 41 members of the principal series, a few each of the sharp and diffuse, and several forbidden lines. Some additions and corrections were made subsequently,[5,6,8-10] and the narrow doublet splittings of the lowest ^{2}P and the first few ^{2}D levels were resolved.[7,8] The lower members of all series are listed in Moore's multiplet tables.[2,3] The energy levels derived from all these sources are listed in full in the National Bureau of Standards 'Atomic Energy Levels', published in 1949.[1] Term values are given for all excited states of the 2*s* electron up to 11*s*, 42*p*, 12*d* and 5*f* respectively. The first four members of both the sharp and diffuse series have been very accurately measured interferometrically by Meissner *et al.*[8] (Certain values for the D-levels quoted in the 1948 edition of 'Atomic Energy Levels' have been subsequently corrected.[9,10])

The doublet splitting in all levels is extremely narrow. Table I gives the values, measured interferometrically, for the 2 ^{2}P and the 3,4,5,6 ^{2}D levels of ^{7}Li; the ^{2}D levels, unlike those of the heavier alkali metals, are not inverted.

TABLE I. - DOUBLET INTERVALS IN THE SPECTRUM OF Li I.

n	2	3	4	5	6
$\Delta\nu(n^2P)$ (cm.$^{-1}$)	0·3366[8] 0·3372[7]	–	–	–	–
$\Delta\nu(n^2D)$ (cm.$^{-1}$)	–	0·037	0·015	0·010	0·005

The value found for the 2 ^{2}P splitting of ^{6}Li is 0·317 cm.$^{-1}$.[7] The question of isotope shifts between lines of the two isotopes is discussed later (see page 272).

Forbidden lines of the 2*s*–*nd*[11,13] and 2*p*–*np*[14-17] series have been found and their intensities measured. In the 2*s*–*nd* series the intensities have been found to agree with those calculated for quadrupole transitions.[12] The appearance of forbidden lines in an external electric field is referred to under Stark effect (see page 271). Two review articles on forbidden lines contain references to the spectra of the alkali metals.[18,19]

The continuous absorption (photoionisation) spectrum of lithium has been investigated in the region 2300 A. to 1850 A.[26,27] The cross-section is found to be $2{\cdot}5 \times 10^{-18}$ cm.^{2} at the series limit and to fall off approximately as $\lambda^{3{\cdot}5}$ below this. Ditchburn *et al.*[28] have compared theoretical and experimental cross-sections for all the alkali metals.

A general account of the experimental determination of line transition probabilities has been given by Mitchell and Zemansky.[29] Measurements on the principal series have been made by direct determination of the lifetime of the excited state[20,21] and by total absorption[22-25] and anomalous dispersion[26] methods. The latest value[25] for the *f*-value of the resonance line is 0·72 ± 0·03, corresponding to a lifetime of 2·8 x 10 sec. for the excited 2 ^{2}P state.

Calculations of intensities in both the line spectrum and the continuum are referred to later (see page 275).

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The Spectrum of Ionised Lithium

Singly ionised.

Lines of the Li II spectrum were early found in discharge tubes[4-6] and in anode rays,[7-10] and their conditions of excitation were studied in various forms of spark and condensed discharge.[11-16] The spectrum was analysed by Schüler[17] and Werner,[18-20] and was shortly afterwards extended farther into the vacuum ultra-violet region by Edlén and others.[21-24] The measured wave-lengths, classifications, and intensities of several of these lines, as far down as 171 A., are also to be found in Moore's multiplet tables.[2,3]

Li II has a helium-like spectrum with the ground-state electron configuration $1s^2\ {}^1S_0$. The ionisation potential is 75·6193 ± 0·0031 V., corresponding to a ground term value of 610,079 ± 25 cm.$^{-1}$.[1] The 43 terms listed in the National Bureau of Standards 'Atomic Energy Levels'[1] incorporate the results of the above-mentioned analyses[17-24] and cover the electron configurations $1s^2$; $1s$ 2-7s; $1s$ 2-6p; $1s$ 3-8d; and $1s$ 4-8f.

The fine structure of the $1s\ 2p\ {}^3P_{0,1,2}$ term has been examined in detail in the course of hyperfine structure measurements (see page 272).

Doubly ionised.

Li III is a hydrogen-like ion, in whose spectrum the first members of the 'Lyman' series (ground state $n = 1$) and the 'Balmer' series (ground state $n = 2$) have been measured.[25,26] 'Atomic Energy Levels'[1] gives the terms derived from these measurements for values of the principal quantum number up to $n = 7$, the fine structure being resolved up to $n = 5$. The ionisation potential for the ^{6}Li isotope is 122·419 V. and for the ^{7}Li isotope 122·420 V., corresponding to term values of the $^2S_{1/2}$ ground state of 987,644·9 cm.$^{-1}$ and 987,657·8 cm.$^{-1}$ respectively.[1]

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Zeeman, Stark, and Pressure Effects

Zeeman Effect.

The Zeeman effect in the alkali metal doublets is described in text-books on spectroscopy (see page 265). Rather fuller accounts have been given by Back and Landé.[1,2] As the historical resumés in these references indicate, the 'anomalous' Zeeman patterns of the resonance lines of the alkali metals played an important part in the development of spectroscopic theory.

The Landé g-factor for the $^2S_{1/2}$ ground state of lithium is 2, and for the $^2P_{1/2}$, $^2P_{3/2}$ levels it is 2/3, 4/3, respectively. In a magnetic field not strong enough to break down the spin-orbit coupling, the Zeeman pattern, in terms of the classical Lorentz splitting $\Delta\nu_L$, consists for the $^2S_{1/2}-{}^2P_{1/2}$ line of two π-components at $\pm\frac{2}{3}\Delta\nu_L$ and two σ-components at $\pm\frac{4}{3}\Delta\nu_L$, and for the $^2S_{1/2}-{}^2P_{3/2}$ line of two π-components at $\pm\frac{1}{3}\Delta\nu_L$ and four σ-components at $\pm\frac{2}{3}\Delta\nu_L$, $\pm\frac{5}{3}\Delta\nu_L$. As the magnetic field becomes strong enough to break down the spin-orbit coupling, the components of both lines merge and tend towards the Paschen-Back pattern, consisting solely of a π-component in the position of the field-free line and σ-components at $\pm\Delta\nu_L$. The Zeeman effect in the alkali metals has been treated mathematically on the basis of Dirac's theory.[8] In lithium the pattern has actually been observed all the way from zero to the strong field case,[3] which is reached, owing to the narrowness of the doublet splitting in lithium, at the relatively low value of about 34,000 gauss. Multiplet structure in the Paschen-Back triplet due to the residual spin-orbit coupling has been resolved and found to agree with the results of calculations.[4-7]

The Zeeman effect in the ground state of lithium has been studied in atomic beam magnetic resonance experiments (see page 273), in the course of which extremely accurate measurements of the splitting have been made. The $g(^2S_{1/2})$ values for lithium, sodium and potassium are found to agree to 1: 40,000.[24] Reasons for small discrepancies have been suggested.[25]

Stark Effect.

The Stark effect is rather briefly discussed in most text-books. A fuller account has been given by Minkowski.[9] The Stark pattern is considerably more complicated than the Zeeman pattern. In the alkali metals the first-order effect is a quadratic one: an asymmetric splitting proportional to the square of the field strength. When unresolved this appears as a simultaneous broadening and shift of the line. The theory has been discussed in several papers.[18-21]

The broadening and shift found in early work on lithium lines was in good agreement with the calculated values.[10-14] In a few experiments the Stark components have actually been resolved.[15-17]

The effect of electric fields on the intensities of forbidden lines in the lithium spectrum has been examined.[22,23]

Pressure Effects.

A general account of the effects of pressure on spectral lines is given by Mitchell and Zemansky,[28] and in 1957 a review article was published by Ch'en and Takeo[29] giving many references to both experimental and theoretical papers on the subject. Some of the most extensive research has been done on the alkali metals, but little of this refers to lithium. In early experiments the broadening of lithium lines in high vapour densities of lithium vapour was compared with the effect to be expected from inter-molecular Stark broadening.[10,12] More recent experiments with high vapour densities have indicated the presence of bands near the series lines in both emission[26] and absorption;[27] these have been ascribed to loosely-bound polarization molecules of Li_2.[27,29]

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Hyperfine Structure and Nuclear Moments

Before the development of magnetic resonance techniques nuclear moments were determined primarily by optical investigation of the hyperfine structure (hereafter referred to as hfs). The theory is given in Kopfermann's book,[1] which also describes the methods used in both optical and radio-frequency spectroscopy. The methods of obtaining nuclear moments are also summarised by Ramsey,[2] with tables of results up to 1952 and many references. Nuclear effects in atomic spectra[34] and the role of nuclear moments in the shell model of the nucleus[36] have recently been reviewed. The data for the lithium isotopes, as quoted by Ramsey,[2] are summarised in Table II. The columns headed $\Delta\nu(2^2S_{1/2})$ refer to the splitting between the two hyperfine levels of the $2^2S_{1/2}$ ground state; this has been measured much more accurately by radio-frequency methods than is possible optically[35] (as has the magnetic moment), but the first few figures of the value converted to cm.$^{-1}$ are given here for convenience. I is the nuclear spin, μ the nuclear magnetic moment (in nuclear magnetons) and Q the nuclear electric quadrupole moment.

TABLE II. - NUCLEAR MOMENTS OF THE LITHIUM ISOTOPES ·

	I	μ(n.m.)	Q	$\Delta\nu(2^2S_{1/2})$ mc/s	$\Delta\nu(2^2S_{1/2})$ cm.$^{-1}$
^{6}Li	1	0·82189 ±0·00004	–	228·208 ± 0·005	0·0076
^{7}Li	$^3/_2$	3·25586 ±0·00011	–	803·512 ± 0·015	0·0268

Optical hyperfine structure in the lithium spectrum is complicated by the isotope shift between components of the two stable isotopes, ^{6}Li and ^{7}Li, and by the narrowness of the fine structure doublet splitting. In the resonance line at 6708 A., for example, the isotope shift and the doublet splitting of the 2^2P level are both of order 0·3 cm.$^{-1}$, while the hyperfine structure (hfs) splitting in the $2^2S_{1/2}$ level is smaller by a factor of about 10. The isotope shift was therefore investigated before the hfs proper, and was indeed first observed by McLennan and Ainslie[4] in 1922 in the resonance line. Their interpretation of the effect was questioned[5-8] until, after further experiments,[9,10] measurements with greater resolution could be made.[11-16] The strong component of the ^{6}Li doublet, however, lies so close to the weak component of the ^{7}Li doublet that the two were not finally resolved until the line was examined in an atomic beam source to reduce the Doppler width; the shifts then found were +0·345 cm.$^{-1}$ and +0·36 cm.$^{-1}$ for ^{7}Li relative to ^{6}Li in the $2^2S_{1/2}-2^2P_{1/2}$ and $2^2S_{1/2}-2^2P_{3/2}$ lines, respectively.[31,32] General accounts of the isotope effect in atomic spectra have been given,[1,34] and Hughes and Eckart[3] have made quantum mechanical calculations for the effect in Li I and II. In very recent measurements with separated isotopes the shift has been measured in a large number of lines besides the resonance line and considerable discrepancies found with the calculations.[37,53]

The isotope shift in the resonance line has been used in spectro-isotopic assays to measure the relative abundance of the lithium isotopes.[17,18]

Hfs was first studied in the $2^3P_{0,1,2}-2^3S_1$ transition of Li II at 5485 A., where the splitting is greater than in the resonance line of Li I. Since

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multiplet splitting, hfs, and isotope shift are all of the same order of magnitude, however, the pattern is a complicated one, in which Schüler resolved 14 components.[19-21] Patterns calculated for various nuclear spin values[22-25] agreed best with the observed structure for $I = 3/2$, $\mu = 3{\cdot}29$ n.m. Further experimental work[26-28] confirmed this assignment.[29] Originally no hfs was found in the ^{6}Li components,[21] but Schüler[28] later found unresolved structure from which he deduced $\mu = +0{\cdot}6 \pm 0{\cdot}2$ n.m. assuming $I = 1$. This early work on the nuclear moments of lithium has been reviewed.[30]

In the resonance line the hfs is due to the splitting into two levels of the $2^2S_{1/2}$ ground state, for the 2^2P splittings are too narrow for resolution, although they can be deduced from displacements. The $2^2S_{1/2}$ splitting was first resolved by Jackson and Kuhn,[31] using an atomic beam source in absorption, and found to be $0{\cdot}0275$ cm.$^{-1}$, in good agreement with the value later found by Meissner *et al.*[32] with an atomic beam in emission, and also with the magnetic resonance value found since.[2] The values deduced from these two experiments for the $2^2P_{1/2}$ splitting are respectively[31] $0{\cdot}0015 \pm 0{\cdot}0009$ cm.$^{-1}$ and[32] $0{\cdot}007 \pm 0{\cdot}002$ cm.$^{-1}$ In the first of these experiments the hfs of the Zeeman effect was also resolved.[31] The later work on optical hfs in all the alkalies and on the hfs of the Zeeman effect has been reviewed.[31,33]

The most accurate measurements of nuclear moments and of the hfs and Zeeman levels of the ground state have been made by radio-frequency methods, mostly in atomic and molecular beams,[1,2,35] although very precise measurements of the magnetic moments have been made in the solid state by nuclear magnetic resonance techniques.[43-46] The spin and magnetic moment of both lithium isotopes were early found by the atomic beam method of zero moments.[38,39] Later, Rabi's magnetic resonance technique was applied to molecular beams of lithium to measure the nuclear magnetic moments with greater accuracy[40] and to atomic beams to measure the ground state hfs and Zeeman effect in both isotopes.[41,42] The ratio of the nuclear *g*-values in the two isotopes has been very accurately measured by the same method and the result ($g_7:g_6 = 2{\cdot}64094 \pm 0{\cdot}00005$) compared with theoretical estimates.[47]

Since the hfs of the $^2P_{3/2}$ state has not yet been resolved, the absolute value of the nuclear electric quadrupole moment is not known for either isotope, although the ratio $Q_6:Q_7$ has been found to be from[51] $2{\cdot}3 \times 10^{-2}$ to[50] $1{\cdot}9 \times 10^{-2}$, the sign of Q being the same for both isotopes.[49] Ramsey quotes in his tables[2] a value calculated by Kusch from molecular beam experiments,[48] but a later paper[52] throws considerable doubt on this calculation, which is therefore not included in Table II above.

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Calculations

Before the development of quantum mechanics, energy levels and doublet splittings in the lithium spectrum were estimated from iso-electronic sequences[1,2] and semi-empirical formulæ[3,4] for both Li I and Li II. Semi-empirical formulæ for certain energy levels and quantum defects have also been given recently.[5-7]

A qualitative quantum-mechanical representation of the two-electron system of Li II was first given by Heisenberg.[8] A full account of the determination of atomic energy levels and eigenfunctions (and hence transition probabilities) is to be found in the book of Condon and Shortley.[9] Hartree in 1946[10] summarised the calculations carried out up to that date on many spectra, including those of lithium from Li^{-} to Li III. The two- and three-electron spectra of Li I and Li II, being the simplest non-hydrogenic spectra, are of particular interest, and a correspondingly large number of calculations has been made on them. The scope of these is indicated briefly here.

Solutions of the Hartree self-consistent field equations with exchange terms were first given for Li I by Fok and Petrashen.[11] Analytic functions both without[12,13] and with[16,17] exchange have been computed for the ground and several excited states of both Li I and Li II by the variational method, and tables of parameters given. Additional papers, some taking into account

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polarization and exchange effects and configuration interactions, give analytic functions for Li I in the ground state[14,15,18-20,27,32] and several excited states,[18,29,32] and for Li II, also in the ground[23,26,28] and some excited[24,25] states. A ten-parameter calculation for Li II is concerned with the Lamb shift in the ground state.[26] Analytic functions taking into account the mutual distances of the electrons have been computed for the ground states of Li I[21,30,31] and Li II,[22] and a perturbation method has also been applied to Li I.[33]

Analytic functions have also been found for the negative ion Li^- by the variational method.[27,34-36] Most of these indicate that the Li^- ion should be stable, with an electron affinity between 0·3 and 0·74 eV.[27,35,36]

Doublet intervals for the ^2P terms have been calculated from both analytic functions[37-39] and Hartree–Fock functions;[40] a few calculations have been made for the ^3P splitting in Li II.[41]

Transition probabilities have been calculated for lines of the principal series with the use of the Hartree field,[42-47] and for lines of all series from Hartree–Fock functions.[48] The intensities of the quadrupole transitions comprising the $2s$–nd 'forbidden' series have also been estimated.[49] The continuous absorption coefficient (photoionisation cross-section) has been calculated by several methods;[42,50-52] in the most recent, using Hartree–Fock wave functions, theoretical and experimental values have been found to agree reasonably well.[52]

A theoretical treatment of the isotope shift in lithium, experimental work on which is discussed above (see page 272) has been given by Hughes and Eckart,[53] and a general treatment of the effect in light elements by Bartlett and Gibbons.[54] Recent experimental work has been compared with the calculated results.[55]

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X-Ray Spectrum

Early work on the *X*-ray spectrum of lithium was concerned mainly with measurement of the *K*- and *L*-absorption edges and their place in the Moseley diagram.[1-3] Energy levels were calculated on the Sommerfeld theory.[4] The results of more recent measurements have been compared with the Moseley diagram[5] and used to compile a table of energy levels.[6] Recent calculations of the absorption edges show fair agreement with experimental results;[8,9] transition probabilities have also been calculated.[7]

Other effects studied include the mass absorption below the *K*-edge,[10] the emission of secondary and tertiary rays,[11] and the Compton scattering of *X*-rays by lithium atoms.[12,13] The scattering has been compared with the results of calculations for both free and bound electrons.[14-16]

With the higher resolution now used in *X*-ray spectroscopy it has been shown that the absorption edges of atoms in the solid state have a fine structure and that, owing to the influence of conduction electrons and neighbouring atoms, many of the emission lines are in fact bands of varying width. Study of these emission and absorption bands gives valuable information about the electronic energy bands in the crystal lattice or among the conduction electrons. In the case of lithium, the fine structure of the absorption edges has been studied in the metal[20,21,27,30] and in compounds.[18,19,27] The positions and widths of many emission and absorption bands have also been measured,[17-19,21-23] and a number of calculations have been made on the subject.[7,24-26,30]

Another recent development in *X*-ray spectroscopy is the production of so-called mesonic *X*-rays (*i.e.*, *X*-rays from an atom in which the radiating electron is replaced by a meson). Information can be derived about both the atomic nucleus and the meson. In lithium, *K*- and *L*-series lines have been identified from π-mesonic atoms.[28,29]

A number of general accounts and review articles discuss the *X*-ray spectrum of lithium with particular emphasis on the importance of *X*-ray spectroscopy in solid-state physics.[31-33]

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THE MOLECULAR SPECTRA OF LITHIUM AND CERTAIN OF ITS COMPOUNDS

By R. F. BARROW

The Lithium Molecule, Li_2

Lithium vapour contains a small proportion of diatomic molecules (about 1% at 1000°K.) which may be detected by means of their absorption spectrum.[1-5] The molecules are observed even on free evaporation from the heated metal into a high vacuum.[17] Three regions of banded absorption have been recognized, in the red,[10,11] blue-green[6,8,9] and near ultra-violet[12-14] regions of the spectrum: the absorption arises from three transitions A,B,C–X, respectively. The A,B–X systems have also been observed in fluorescence,[3] and the B–X system in magnetic rotation.[8] In the case of this $^1\Pi$–$^1\Sigma$ system, only the lines near the band-origins appear, so that the spectrum looks like an absorption spectrum with very low rotational, but not vibrational, temperature. The reduced overlapping of lines of course facilitates the analysis. The A,B–X systems have been investigated in great detail, and the isotope effect between $^7Li_2$ and $^7Li^6Li$ has been studied very thoroughly.[10,11] The band-lines of the molecule $^7Li_2$ show alternating intensity: the nuclear spin of ^7Li is found[6,7] to be 3/2. Measurements of the anomalous dispersion near absorption lines of the red system have been made;[16] they lead, however, to an incorrect value of the nuclear spin. The analysis of the red system, $A^1\Sigma_u^+$–$X^1\Sigma_g^+$, shows that there is a small electronic isotope shift:-

$$\nu_e^i(^6Li^7Li) - \nu_e(^7Li_2) = -0{\cdot}064 \pm 0{\cdot}010 \text{ cm.}^{-1} \text{ (reference 10)}$$
$$-0{\cdot}054 \pm 0{\cdot}009 \text{ cm.}^{-1} \text{ (reference 11)}$$

(For a theoretical treatment of this effect, see reference 18).

The ultra-violet bands are less well known; no rotational analysis has yet been made, and there is some doubt whether the bands form more than one system. The most likely view is that state C is $^1\Sigma_u^+$, which gives, on dissociation, $Li(2^2S_{1/2}) + Li(3^2P)$. Other diffuse bands at shorter wave-lengths have been reported.[15]

The dissociation energy of Li_2 was measured by Lewis,[19] who used a beam in which the atoms were separated from molecules by an inhomogeneous magnetic field. The concentration of atoms was then determined by ionization on a tungsten filament and measurement of the positive-ion current. Lewis's results were supported by later work;[20] recalculated,[35] they lead to $D_0''(Li_2) = 25{\cdot}68 \pm 0{\cdot}15$ kg.-cal.mole.$^{-1}$ A very slightly higher value, 25·8 kg.-cal., is obtained[21] by extrapolation of the vibrational intervals[8] in the state $B^1\Pi_u$. It is possible that there is a real difference here, representing the height of a maximum[22] in the potential energy curve for the $B^1\Pi_u$ state.

Values of the spectroscopic constants for $^7Li_2$, taken from Herzberg[23] are given in Table III. Qualitative discussions of the lower excited electronic states have been given by Hund[24] and Mulliken.[25] The ground state is formed from ground-state atoms; the states A and B dissociate to give $Li(2^2S_{1/2}) + Li(2^2P)$. (Potential energy–distance curves are given by Mulliken[25] and Herzberg[23]). Quantitative wave-mechanical treatments of the Li_2 molecule have also been given; a Heitler-London calculation[26] gives $D_0'' = 26$ kg.-cal. and

TABLE III. - SPECTROSCOPIC CONSTANTS FOR $^7Li_2$

State	T_0	ω_e	$x_e\omega_e$	$y_e\omega_e$	B_e	α_e	r_e, A
$C^1\Sigma_u^+$	30498·8	231·5	1·5				
$B^1\Pi_u$	20395·96	269·69	2·744	−0·0637	$0{\cdot}5572_3$	$0{\cdot}0080_4$	$2{\cdot}936_4$
$A^1\Sigma_u^+$	14020·62	$255{\cdot}45_6$	1·574	+0·0018	0·49749	0·00541	3·1077
$X^1\Sigma_g^+$	0	$351{\cdot}43_5$	2·592	−0·0058	$0{\cdot}6727_2$	0·00704	2·6725

$r_e'' = 2{\cdot}4$ A. This treatment fails,[27] however, for the state $B^1\Pi_u$. A later calculation[28] gives $D_0'' = 27$ kg.-cal.

An accurate potential function for the ground state has been given.[29] It rises more steeply at $r > r_e$ than the Morse curve: the maximum difference is about 1 kg.-cal. The applicability of the simple potential function $V = (a/r^m) - be^{-nr}$ has been considered.[30] Relations between the force constant, equilibrium distance and dissociation energy have been discussed.[31-34]

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Mixed Alkali-Metal Molecules Containing Lithium

Electronic spectra of the mixed molecules LiK, LiRb and LiCs have been investigated in absorption with low resolving power.[1] Analyses have been given,[2] but the values of the constants, given in Table IV, are subject to a good deal of uncertainty. Attempts to observe an absorption spectrum of LiNa have been unsuccessful.[1,3]

TABLE IV. - SPECTROSCOPIC CONSTANTS FOR MIXED ALKALI-METAL MOLECULES

	LiNa	LiK	LiRb	LiCs
T_0(B), cm.$^{-1}$	–	17540	17500	16432
ω'(B), cm.$^{-1}$	–	126	81	77
ω''(X), cm.$^{-1}$	(252)	207	185	167

The value given for ω'' for LiNa is an estimate.[4]

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Lithium Hydride, LiH

A many-line spectrum of bands degraded to longer wave-lengths, and lying in the region 3000 to 4500 A., was observed by Watson.[1] It arises from a transition $A^1\Sigma^+$-$X^1\Sigma^+$ in LiH, (V-N in Mulliken's nomenclature), and has been observed both in absorption, and in emission in arcs or discharge tubes. Following a preliminary analysis[2] and examination of the isotope effect[3] between ^{7}LiH and ^{6}LiH, the system was studied by Crawford and Jorgensen,[4-7] who have given a detailed account[5-7] of the isotope effect between $^7Li^1H$ and $^7Li^2H$. They also report a second system, perhaps of triplet bands, in the red region of the spectrum,[4] but this system does not appear to have been studied further. A third system, observed[22] in absorption in the ultra-violet region of the spectrum, arises from the transition $B^1\Pi$-$X^1\Sigma^+$. Values of the constants[6,22] for states B, A and X are given in Table V.

TABLE V. - SPECTROSCOPIC CONSTANTS FOR LiH

State		T_0	ω_e	$x_e\omega_e$	$y_e\omega_e$
$^7Li^1H$	$B^1\Pi$	34312·26	215·5	42·4	–
	$A^1\Sigma^+$	–	234·41$_3$	–28·947	–4·185*
	$X^1\Sigma^+$	0	1405·65	23·20	0·1633
$^7Li^2H$	$B^1\Pi$	34466·27	177·28	29·13	–
	$A^1\Sigma^+$	–	180·711	–13·987	–1·1784*
	$X^1\Sigma^+$	0	1055·12	13·23	0·13
		B_e	α_e	γ_e	r_e, A
$^7Li^1H$	$B^1\Pi$	3·383	0·986	0·045	2·378
	$A^1\Sigma^+$	2·8186	–0·07831	–0·02627*	2·596
	$X^1\Sigma^+$	7·5131	0·2132	$7\cdot5 \times 10^{-4}$	1·5954
$^7Li^2H$	$B^1\Pi$	1·908	0·427	0·006	2·376
	$A^1\Sigma^+$	1·6060	–0·01450	$-1\cdot844 \times 10^{-3}$*	2·586
	$X^1\Sigma^+$	4·2338	0·09198	$6\cdot7 \times 10^{-4}$	1·5949

* Higher terms known.

The significance of the signs in this Table may be illustrated as follows:-

For $X^1\Sigma^+(^7Li^2H)$: $G_v = 1055\cdot12u - 13\cdot23u^2 + 0\cdot13u^3,$
$B_v = 4\cdot2338 - 0\cdot09198u + 6\cdot7 \times 10^{-4}u^3,$

where $u = v + \frac{1}{2}$; see also Herzberg.[8]

The constants for the two isotopic species are not, as they are for heavier molecules, exactly related by the appropriate power of the ratio of the reduced masses; that this is so arises from the neglect, in the simple treatment of molecular energy levels, of certain terms,[9] including anharmonicity terms due to the interaction of rotation and vibration.[10]

The upper electronic states, $A^1\Sigma^+$, are, as is the case for the other alkali metal hydrides,[11] 'quite abnormal in that the molecules appear to *shrink* in size as well as to vibrate more rapidly as the amount of vibrational energy increases'.[7] This is attributed to the existence of a relatively low-lying state[12] which correlates with Li^+H^-. The ground state is strongly polar near

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the equilibrium configuration, but finally goes over into neutral atoms Li(^{2}S) + H(^{2}S) with increasing internuclear distance. The excited state, however, is only partially ionic in character near its minimum, becoming at larger internuclear distances largely ionic (Li^+H^-), and finally[13] going over into neutral atoms Li(^{2}P) + H(^{2}S).

The states $B^1\Pi$ are very shallow states correlating with Li(2p^{2}P) + H or D. Breaking off of the rotational structure of the levels in the $B^1\Pi$ state is attributed to predissociation by rotation; the observations lead to accurate values of the dissociation energy, D_0(LiH) = 56·01$_5$ ± 0·005 kg.-cal., D_0(LiD) = 56·525 ± 0·023 kg.-cal. Several theoretical treatments of the binding in the LiH molecule have been given. Heitler–London calculations give not much more than half the correct dissociation energy.[14,15] In a two-electron calculation,[16] the dipole moment was estimated to be 3·5 D., but a later, four-electron calculation[23] gives the result μ = 6·04 D. (hydrogen negative) (see also [24,25]). A treatment of the LiH^+ molecule indicates that this is unstable,[17] but in a molecular-orbital calculation, Knipp[18] obtains a dissociation energy as high as 2·$_0$ eV. for LiH, and finds that the ground state of LiH^+, $^2\Sigma$, is stable, with r'' ~ 1·6 A. A more empirical discussion of the binding in the alkali hydrides has proved successful. A molecule is treated as consisting of ions, each of which is polarized by the electrostatic field of the other.[19] Good agreement is obtained between the experimental and calculated binding energies.

Variations in the spectroscopic properties of the alkali metal hydrides have been reviewed by Pearse;[11] more general variations are discussed, for example, by Sheline.[20]

Intensity measurements in the hydride spectrum may be used to determine the ^{6}Li/^{7}Li ratio.[21]

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Lithium Halides: Gaseous

Accurate values of the rotational constants of the gaseous molecules have been obtained for lithium bromide and iodide from their spectra in the microwave region.[1] Observations of the Stark effect, leading to values of the dipole moments, have also been made. The magnitudes of the quadrupole coupling constants indicate that the gaseous molecules are, as expected, highly ionic.[21] Thus, for LiBr and LiI the ratios of the observed coupling constants to those expected for covalent bonds are[1] 0·048 and 0·086, respectively. Important information about the properties of gaseous lithium fluoride[13] and chloride[16] has been obtained from the molecular-beam electric resonance spectra.[23] Rotational Stark transitions $J,m_J \rightarrow J,m_{J'}$ in lithium fluoride have been studied by the same technique.[17] The absorption spectra of lithium chloride, bromide and iodide have also been studied in the vibration-rotation region.[2] Only broad, unresolved bands are observed, but they suffice for the determination of the fundamental vibration frequencies. No indication of the presence of dimers was found in these investigations, although several different lines of evidence, e.g. from mass-spectrometric[3] studies, molecular beams[4] and vapour pressure,[5] show that the alkali halide vapours, like those of the hydroxides, do not always consist solely of monomeric species.

The visible or ultra-violet spectra of the gaseous alkali halides arise by transitions from the ground state, $X^1\Sigma^+$ in all cases, to one or more excited states correlating with the neutral atoms. Little is yet known in detail about these excited states. They are repulsive, or at the least possess small minima, so that the spectra are either continuous, or show fluctuation bands.[6-8,15,18] It seems likely[9] that the strongest continuum at shortest wavelength is a transition $0^+ \leftarrow X^1\Sigma^+$, while the fluctuation bands at longer wavelengths arise from the transition $1 \leftarrow X^1\Sigma^+$. The spacing of the fluctuation bands reflects the spacing of the vibrational levels in the ground state and the slope of the potential energy-distance function for the excited state. Thus, by making certain assumptions, it is possible from measurements of the fluctuation bands to derive estimates not only of the vibration frequencies in the ground states but also of the dissociation energies.[6,7] However, the dissociation energies of these molecules are now best determined thermochemically according to the equation:-

$$D(\mathrm{MX}) = -Q_f(\mathrm{MX}) - \Delta_s H(\mathrm{MX}) + \Delta_s H(\mathrm{M}) + \tfrac{1}{2}Q_f(\mathrm{X})$$

where $D(\mathrm{MX})$ is the heat of dissociation of the halide MX into ground-state atoms, M and X;

Q_f is the standard heat of formation, and

$\Delta_s H$ the heat of sublimation.

Likewise the most reliable values of the vibration frequencies are probably those determined from the infra-red spectra.

The ultra-violet absorption spectrum of gaseous lithium fluoride has not yet been observed; work on the other lithium halides has been reported as follows; lithium chloride,[8,14] lithium bromide,[8] lithium iodide.[6,8,15]

A discussion has been given of the effect on the dipole moment of isotopic substitution,[19] and the measurement of mass ratios[20] from microwave spectroscopic information has been considered.

Values of the spectroscopic constants of the gaseous lithium halides are given in Table VI.

TABLE VI.- SPECTROSCOPIC CONSTANTS FOR THE GASEOUS LITHIUM HALIDES

Molecule	B_e [b]	α_e [b]	r_e, A	$\omega_e$cm.$^{-1}$	μ, D.
LiF	-	-	[1·527][e]	720[f]	6·6[13]
LiCl	-	-	[2·022]	662[2]	-
LiBr	19162·32[c]	208·8[c]	2·170$_4$	576[2]	6·19 ± 0·15
LiI	15381·99[d]	152·6[d]	2·391$_9$	501[2]	6·25 ± 0·20

Notes.
- a. The values are taken from reference 1, except where otherwise indicated. Values in square brackets are estimated values.
- b. The values of B_e and α_e are in Mc./sec.
- c. Constants for ^{6}Li^{79}Br.
- d. Constants for ^{6}LiI.
- e. According to [13], r_0(^{7}LiF) = 1·51 ± 0·08 A.
- f. This figure for ^{6}LiF is the mean of two discordant observations,[13] ω_e(^{6}LiF) = 756 ± 38 cm.$^{-1}$, ω_e(^{7}LiF) = 646 ± 32 cm.$^{-1}$

Dissociation Energies, D_{298}, kg.-cal.mole^{-1}

	LiF	LiCl	LiBr	LiI
$-Q_f$(MX)	146·3[10]	97·70[10]	83·72[10]	64·79[10]
$-\Delta_s H$(MX)	-66·3[5]	-48·$_0$*	-46·$_1$*	-44·5[3]
$\Delta_s H$(M)	38·44[11]	38·44	38·44	38·44
½Q_f(X)	18·86[a]	29·01[10]	26·71[10]	25·48[10]
D_{298}	137·3	117·$_2$	102·$_8$	84·2

* Estimated, from figures given by Kelley.[12]

a. Recalculated, from [22]

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COMPOUNDS OF LITHIUM: SOLID STATE

Lithium Hydride

The ultra-violet absorption spectra of thin layers of the hydride and deuteride have been observed.[1-3] Maxima were first found at 2517 and 2482 A., respectively,[2] but in later work[3] no maximum was found at $\lambda > 1860$ A. The elementary photochemical process is considered to be an electron jump from the anion to the cation within the lattice (see page 285 and ref. 5 on page 286).

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Lithium Hydroxide

The infra-red absorption spectra of thin sheets of solid LiOH and LiOH,H$_2$O have been examined for the normal, partly deuterated and fully deuterated compounds. It is concluded[1] that both hydrogen atoms from each water molecule are used in forming strong hydrogen bonds in the hydrate. The fundamental vibration frequency of OH$^-$ in LiOH was found to be 3839 cm.$^{-1}$

Reference

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Lithium Oxide, Li$_2$O

The dispersion in the ultra-violet region has been examined.[1]

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Lithium Halides

In order to avoid repetition, certain properties of the crystalline alkali metal halides are discussed in detail under only one appropriate alkali metal, as follows: ultraviolet absorption spectra, page 285; Raman spectra, Sect. XXXIX; colour centres, luminescence and phosphors, under the spectra of potassium halides.

The alkali-metal halide crystals, like other ionic crystals, absorb radiation both in the infra-red and in the ultra-violet regions at characteristic frequencies.

In the infra-red, the characteristic frequency corresponds to the maximum frequency of lattice vibration in which the positive and negative ions move in opposite directions. These frequencies may be calculated from other properties of the crystal.[1,2] The observed widths of the absorption bands are, however, far greater than those calculated according to a simple model, and the transmission curves often show a structure, suggestive of the presence of more than a single absorption line.[3,22-24]

The longest-wave-length absorption band in the ultra-violet region of the spectrum is considered to arise from the transition:-

$$M^+ + X^- + h\nu \rightarrow M + X$$

in which an electron is transferred from a halogen ion to a neighbouring cation. The energy required for this process may be evaluated as follows:-[4]

	Work done
(1) A negative ion is removed from a normal site in the lattice to infinity	$\alpha \mathbf{e}^2/r$
(2) An electron is removed from this ion	E
(3) The neutral halogen atom is replaced in the vacant lattice site	0
(4) An adjacent positive ion is removed to infinity	$(\alpha-1)\mathbf{e}^2/r$
(5) An electron is added to the positive ion	$-I$
(6) The neutral alkali atom is replaced in the vacant lattice site	0

Here α is the Madelung constant, **e** the electronic charge, r the smallest anion–cation distance in the lattice, E the electron affinity of the halogen atom and I the ionization potential of the alkali atom. The total work done is:-

$$\begin{aligned} W &= (2\alpha-1)\mathbf{e}^2/r + E - I, \\ &\equiv Q + E - I, \end{aligned}$$

where Q is the coulomb part of the lattice energy. The values of W calculated in this way are higher[21] than the observed values of $h\nu$, but inclusion of the changes in the polarization energy caused by the electron transfer improves the agreement.[5] Further improvement results when account is taken of the interactions of the atoms, particularly of the alkali atom, with the neighbouring ions, and there is little doubt that this process describes correctly the transition in the longest-wave-length ultra-violet absorption band (for a discussion of the shorter wave-length bands, see, for example [3,25]).

The infra-red absorption maximum for lithium fluoride[6] lies at 32·6 μ.

In the ultra-violet region, maxima have been located[7-9] as follows:-

LiF	<1100 A.	LiCl	1430 A.	LiBr	1730 A.	LiI	2120 A.
			1300		(1620)		1970
					1560		(1830)
							1760
							(1670)
							(1400)
							(1200)

The reflexion of electrons at crystalline films of the alkali halides is minimal for electron energies corresponding to the known limits of optical transparency.[27] The reflectance of lithium fluoride in the region 1200 to 2000 A. has been measured.[28]

Lithium fluoride is an important optical material: in the infra-red its transparency[10-12] limits its use to $\lambda \leqslant 5\cdot3\ \mu$, but in the Schumann region it absorbs little[13-15] until about 1300 A., and good samples may transmit useful amounts of radiation at wave-lengths of about 1100 A. On account of this property, it finds a use as a material for windows, lenses and prisms for the spectroscopy of the vacuum ultra-violet region.[15] It may also be employed in achromatic lens combinations to cover a wide spectral region.[16] An X-ray spectrograph using a lithium fluoride crystal has been described.[17]

A theoretical treatment of the Raman spectrum of crystalline lithium fluoride has been given,[18] but this has by no means found universal acceptance[19] (see also Sect. XXXIX).

The Raman spectrum of aqueous lithium chloride indicates a high degree of dissociation; no spectrum other than that of water is observed even in 13N. solutions.[20] Enolization in solutions of lithium bromide in acetone has been studied[26] by observations of their infra-red absorption spectra.

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Colour Centres

In the section on the spectra of potassium halides some mention is made of colour centres in the crystals of the alkali halides. Investigations of colour centres and luminescence have also been reported for the lithium halides, particularly lithium fluoride. This substance, however, shows unique characteristics,[1] some of which may arise from traces of impurities. Reference may be made to the following reviews[1-4] and papers.[5-11]

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Lithium Sulphate

Both the Raman[1,2] and the infra-red[3] spectra of crystals of Li_2SO_4,H_2O have been studied.

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Lithium Carbonate

The infra-red spectrum of lithium carbonate has been obtained by the powder method.[1]

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Lithium Nitrate

A study[1] of the Raman spectra of solid $LiNO_3,3H_2O$ and of its aqueous solutions leads to the conclusion that there is incomplete dissociation in solutions more concentrated than about 0·5N. The infra-red[2] and ultra-violet[3] spectra have also been examined.

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Lithium Phosphates

Infra-red powder absorption spectra have been recorded[1] for Li_3PO_4, $Li_4P_2O_7,2H_2O$, Li_2HPO_3,H_2O and LiH_2PO_2.

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SECTION XX

THE ANALYTICAL DETERMINATION OF LITHIUM

By H. V. THOMPSON

DETECTION

In the detection of lithium by wet tests the usual procedure is first to prepare a solution containing only the chlorides of the alkali metals and, if necessary, further concentrate the lithium by taking advantage of the much greater solubility of anhydrous lithium chloride in various organic solvents (see below). Alternatively, picrolonic acid has been recommended,[1] as it precipitates sodium, potassium, ammonium and the alkaline earths, but not lithium. Formerly, lithium was generally detected by precipitation of its relatively insoluble phosphate, fluoride or carbonate,[2] but other reactions are now available including the use of an ethereal solution of ammonium stearate,[3,4] hexamethylenetetramine in the presence of potassium ferricyanide,[4-7] alizarin Red S,[4,8] alkali metal arsenite in methyl or ethyl alcohol[9] and precipitation as the acid aluminate,[10] or in alkaline solution as lithium potassium ferric periodate.[11,12] With a number of azo dyes, lithium salts give colour reactions in alkaline solution which are said to be highly sensitive;[13,14] fluorescence tests for the detection of lithium have also been described.[15,16] After separation of the alkali metals by paper chromatography lithium is detected on subsequent development of the chromatogram.[16a] A physical test, claimed to be sensitive to 10^{-6}g. of lithium, depends on the action of molten lithium salts on soda-lime glass, whereby the sodium ions in the glass are replaced by lithium ions from the molten salt and the glass becomes superficially fractured and opaque.[17]

When present in mere traces lithium is best detected spectrographically. As a general rule reliance is placed on simple spectroscopy, *i.e.* the old-established flame test, to indicate the presence of lithium before any confirmatory tests are undertaken, and in applying this test the sensitivity can be much enhanced by the use of a filter,[18] 2 cm. in thickness, consisting of an aqueous solution of coccinin (0·14%), Dahlia Violet (0·0014%) and $CuSO_4,5H_2O$ (0·7%).

DETERMINATION BY CHEMICAL METHODS

Gravimetric methods.

In the standard gravimetric processes for the determination of lithium, the mixed alkali chlorides are obtained in a solution from which all other metals and acid radicals, as well as ammonium salts and organic matter, have been eliminated. After evaporation and drying, the mixture of anhydrous chlorides is extracted with an organic solvent or solvents in which only lithium chloride is significantly soluble. Among such solvents are amyl alcohol,[19-27] ethyl alcohol-ether,[24,28-32] *iso*butyl alcohol,[33-35] 2-ethylhexanol,[36] acetone[37-39] and dioxan.[40] Other solvents have also been recommended.[41,42]

Although such a variety of solvents is available, in practice the choice narrows considerably, and it seems probable that in most determinations either Gooch's amyl alcohol process[19] is used, or extraction with a mixture of alcohol and ether by Palkin's modification[29] of Rammelsberg's original method[28] is employed.

The lithium chloride thus separated is often converted into sulphate and weighed as such;[27,42,104,105] alternatively the lithium may be determined as lithium zinc (or nickel) uranyl acetate.[27,43-47,104] Another procedure is to treat a mixture of sodium and lithium perchlorate, dissolved in anhydrous *n*-butyl alcohol, with a solution of hydrogen chloride in *n*-butyl alcohol, when the sodium perchlorate is converted into chloride and the lithium salt, which alone remains in solution, is determined as sulphate.[48,49]

A method recently described for the determination of microgram quantities of lithium in the presence of excess of sodium and potassium salts involves precipitation as the complex $2Li_3Fe(CN)_6,K_3Fe(CN)_6,5(CH_2)_6N_4,6H_2O$ from an acetone-water mixture.[50] Other methods proposed for the determination of lithium are as the fluoride,[23,51-54] the phosphate[27,55] and the aluminate,[27,42,56,57,104] $2Li_2O,5Al_2O_3$. Ion exchange chromatography has been applied to separate lithium from sodium and potassium and the lithium can then be determined by any appropriate method.[57a]

Volumetric Methods.

The volumetric determination of lithium is limited in scope and none of the few suggested processes has gained any substantial measure of general acceptance. Solvent extraction of lithium from a mixture of the anhydrous alkali metal chlorides enables the lithium to be determined by a Volhard titration.[36] In the periodate process lithium is precipitated either as such or as lithium potassium ferric periodate, $LiKFeIO_6$, and, after adding an excess of potassium iodide to an acid solution of the washed precipitate, the liberated iodine is titrated.[58-60] Other suggested procedures are to convert the lithium salt into borate with subsequent titration of the boric acid;[40] and a difference method based on the conversion of the mixed alkali chlorides into carbonates and titration of aliquot portions of the solution before and after removing the lithium carbonate.[61] If isolated as lithium zinc uranyl acetate, lithium can be determined volumetrically by the method used for sodium (see Sect. XL).

DETERMINATION BY PHYSICAL METHODS

Polarography.

A direct determination of lithium is possible by polarographic methods,[62-64] because its half-wave potential is sufficiently far removed from those of the other alkali metals to give a simple and not a cumulative wave in mixed solutions.[65-67] The usual practice is to carry out the determination with aqueous tetraethylammonium hydroxide as the supporting electrolyte in an aqueous solution of alcohol containing only the alkali chlorides, provided that not more than a ten-fold excess of sodium or potassium is present;[67] otherwise a preliminary concentration of the lithium is necessary.

Flame Photometry.

When lithium is present neither as a trace element nor as a dominant constituent, the modern technique of flame photometry certainly provides the quickest method for the determination of lithium:[68-77] it is probably as precise as any and has been found particularly useful in the analysis of silicates. Such materials are first evaporated almost to dryness with hydrofluoric and sulphuric acids and from the fluoride-free residue an acid solution containing only metal sulphates is obtained. When this solution is atomized in the coal-gas burner of a simple flame photometer provided with a suitable interference filter, lithium can be accurately determined in the presence of at least a ten-fold excess of sodium, potassium or calcium, and predominant quantities of aluminium do not interfere. However, with other types of material, according to their composition, it may be necessary to remove certain of the cations before the solution is atomized.

Spectrography.

A considerable volume of work has been published on the spectrographic determination of lithium and, although this method is not necessarily restricted to determining traces of lithium, it is particularly valuable when the concentration of the element is below the effective limit of chemical methods.

An approximate determination accurate to about 0·001 mg. of lithium can be made by the progressive dilution of a prepared solution until the line 6708 A. is either just visible or just fails to appear when the flame is viewed through a simple spectroscope.[78,79] For more precise work or smaller quantities of lithium, arc,[80-86] spark[87-90] or flame[91-98] spectrum methods must be used, the actual determination being usually made by an internal standard technique or by a simple comparison standard procedure.

Colorimetry.

When lithium has been separated as its complex ferric periodate (see page 289), the iron in the precipitate can be determined colorimetrically.[99] The colorimetric process used for determining sodium after precipitation as its triple acetate (see Sect. XL) is applicable in the same circumstances to lithium.

Reagents for the detection and determination of lithium are dealt with in a number of reviews on the analytical chemistry of the alkali metals.[100-103]

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SECTION XXI

BIOLOGICAL PROPERTIES OF LITHIUM

By F. CALL

Effect on vegetation

Since lithium is widely though sparsely distributed in soils, it is not surprising that it is found to be present in most plants. Quantitative spectrographic determinations have been carried out on a large number of species and collected data are available.[1-8] The content varies from 0·09 to 9·5 parts per million on a dry weight basis, averaging 1·29p.p.m. for cryptogams and 2·06 for phanerogams. The *Gramineae* (grasses and cereals) and *Liliaceae* are poorest, the lowest content, 0·09p.p.m., found being in the pollen of the lily. The stalk, ovaries and anthers had less than 1p.p.m. but the leaves and petals contained up to 2·5p.p.m. The roots usually have a higher lithium content than the aerial parts of the plant, while the phloem exudate of species of *Fraxinus*, *Platanus*, *Robinia* and *Cucurbita* was often richer in lithium than the parenchyma sap.[9] The element was also present in the skin of the mushroom.[10]

Plants grown in soils rich in assimilable lithium varied widely in the amounts taken up; thus alfalfa takes up very little and tomato a great deal.[11] This suggests that plants may differ greatly in their ability to absorb lithium. The rate of absorption by rice of lithium from aqueous solutions actually decreased as the concentration of the solution increased[12] while the rate of absorption by *Chara ceratophylla* increased, but not proportionately, being stimulated by light and not attaining equilibrium in fourteen days.[13] There was no loss of lithium from the latter species on transfer to lithium-free solutions but with wheat, although lithium in the older leaves appeared to be immobile it was readily lost from the roots.[14] In contradistinction to the distribution found in plants grown in soil,[2] sixteen species grown in nutrient solutions had a higher content of lithium in the shoots than in the roots.[15] No significant differences were found in the distribution or content of lithium in lentils grown in different soils.[16] The cotyledonous leaves of the broad bean are able to absorb lithium but not barium or thallium from aqueous solution[17] and a similar selective absorption is shown by some fruits.[18] Lithium was found to be transported vertically in the woody stems of the willow, being, unlike water, unable to pass laterally across the stem.[19] Kinetic studies of the absorption of alkali cations by barley roots indicated that lithium was not competitive with potassium or rubidium but in fact increased the rate of absorption of rubidium.[20] The amounts of lithium taken up by other plants could not be correlated with the uptake of other cations, the ratio varying with age of plant, species and a number of other factors.[21-24] Substitution of equivalent amounts of lithium for potassium resulted in decreased yields of wheat and the plants died as soon as potassium had been completely substituted.[25] The lithium content of walnut trees was found to be independent of the presence or absence of manganese deficiency.[26]

At low concentrations lithium has a definite stimulating effect on the germination of many seeds[27-29] and on the subsequent growth of the seed-

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lings.[30-33] Although a very productive soil has been found to be characterised by the presence of lithium among other elements,[34] reduction of the pH of such a soil may result in the absorption by plants of toxic amounts of lithium.[35] At higher concentrations lithium is the most toxic of the alkali metals[36,37] and has been shown to be responsible for a specific mottle leaf disease in citrus.[38-40] The application of carefully regulated doses of lithium salts gives effective control of many bacterial and fungal diseases of plants, notably of powdery mildew, *Erisyphe sp.*[41-48] There have been a number of attempts to discover a fundamental effect on the plant cells of lithium among other alkali metals by cytological methods,[49-53] permeability measurements[54-56] and determinations of membrane potentials[57] but the results are largely inconclusive.

Effect on Micro-Organisms

Bacteria, and especially actinomycetes and fungi, in soil are stimulated by the addition of lithium salts.[58] Lithium chloride can be substituted for sodium chloride in the culture of *Vibrio costicolus*[59] and it has been suggested that lithium may be an essential factor for growth in the symbiosis of *Rhodotornia rubra* and *Mucor ramanianus.*[60] In higher concentrations lithium salts are, however, definitely toxic to fungi.[61] The toxicity of lithium halides to *Penicillium italicum* was found to increase with the atomic weight of the halogen and there was some indication that the lithium ion was relatively non-toxic,[62] but the metallic ion appeared to be the toxic agent in the case of the slime moulds, myxomycetes.[63] Lithium has been included in a number of investigations of the toxic effects of metals on bacteria.[64-72] In a paper covering thirty nine different species of bacteria and fungi, lithium was reported to be the most toxic alkali metal after caesium for both bacteria and fungi.[64] The action was bacteriostatic rather than bactericidal and lithium was in fact slightly superior to cæsium as a bactericide at high concentration. The toxicity of lithium ions to three organisms was markedly decreased by reducing the pH of the medium from 6·5 to 5·0.[72,73] An interesting property shown by lithium salts is that of inducing morphological changes in bacteria,[73-79] manifested by different habits of growth. Thus *Chromobacterium violaceum* forms atypical secondary colonies of large papillae,[73] *Escherichia coli* changes to vacuolated amoeboid forms[75] while *Aerobacter aerogenes* changes from a ropy to a non-ropy form.[78]

These changes may be associated with changes in the permeability of the bacterial cell wall.[74] One interesting suggestion is that the changes are due to accumulation of metabolic products which lower the pH of the medium, thus causing the lithium ion to become more toxic to the parent than to the secondary form.[73]

Similar morphological changes have been observed in algae,[80] while strains of brewer's yeast, *Saccharomyces cerevisiae*, have been found to grow successfully in normal lithium chloride solution, the resistant mutant being dominant.[81] Lithium salts cause reversal of the beat of the cilia of the protozoon *Paramecium*, the adaption taking about 18 hr.; but no tolerance to toxic concentrations of lithium halides could be induced in this species by exposing the organism to sub-lethal concentrations.[83] Lithium salts gave some protection to *Paramecium* against injury by freezing[84] and were less toxic to *Spirogyra* than sodium or potassium salts.[85] The rate of absorption of bacteriophage by *Escherichia coli* was increased by low concentrations of lithium salts but depressed by higher concentrations.[86]

Lithium in Marine Organisms

Although lithium is present in sea water there has been little study of the uptake by marine organisms, but the element has been shown to be present in the common brown algae, *Laminariaceae* and *Fucaceae*[87] and in the embryo of the cephalopod, *Sepia officinialis.*[88]

Effect on Animals

(*a*) Distribution

The widespread occurrence of lithium in plants suggests that it would also occur in animals and a study of the ash of thirty seven samples of invertebrates, fish, batrachians, reptiles, birds and mammals, shows that lithium is present in all except turkey egg yolk.[89] Invertebrates generally contain more, 0·05 to 5·8mg./kg. dry ash, than vertebrates, 0·024 to 0·77mg./kg. The element has also been identified in the ash of dog liver,[90] most organs and tissues of the white rat,[91] silkworm larvae,[92] and guinea-pigs.[93] Lithium is said to occur spasmodically in human tissues[94] but it has been found present in 95·7% of specimens examined of reproductive organs, stomach, thyroid and placenta, and in hydatid cysts,[95,96] to the extent of 0·01 to 0·1% of the ash. It also occurs in the brain,[97] in tumour tissue[98] and in blood where it is largely confined to the plasma, the content ranging from 9 to 30mg./l., with an average of 19mg./l.[99] Although lithium was found to be present as the phosphate in human teeth and bone,[100] a later investigation found no trace in bone specimens from thirty three individuals.[101]

The element is usually present in human milk and cows milk,[102-105] although sometimes absent,[103] and in eggs.[106] Although ingested lithium salts are absorbed and rapidly excreted in the urine, lithium in natural foods is poorly absorbed.[107]

(*b*) Effect on Enzyme Systems.

The effect of lithium on enzyme systems has been summarized.[108] In general the lithium ion behaves as an activator but its role is not clear cut and the anion may play an important part. Thus although lithium sulphate has a specific inhibiting effect on acid liver phosphatase,[109] other salts of lithium may enhance the action of this enzyme system.[110] Lithium salts of ester phosphates are split by slightly acid phosphatase[111] as is lithium acetyl phosphate by the appropriate enzyme.[112] The metabolism of octanoic acid by liver slices is greatly stimulated by lithium ion[113,114] but there is only a slight effect on the respiration of mitochondria in the presence of Krebs cycle intermediates.[115] Weak activation also occurs with deoxyribonuclease,[116] human serum hydraluronidase[117] and alfalfa pectinesterase.[118] Lithium has a negligible effect on the formation of amylase by *Aspergillus oryzae*[119] and cannot replace sodium in stabilizing the activity of plant carbonic anhydrase.[120] Definite though weak inhibition occurs with the lipase of the castor oil plant,[122] urease,[123] plant peroxidases,[124] pepsin,[125] tryptophanase,[126] succinate decarboxylase[127] and the acetate-activating enzyme system.[128] Lithium has no effect on tyrosinase action.[129]

(*c*) Effect on Animal Tissues.

The conversion of fibrinogen to fibrin is inhibited by lithium salts though not so effectively as by calcium salts.[130 132] Solutions of lithium chloride or bromide in the absence of calcium are, however, able to dissolve fibrin clots to form fragments resembling fibrinogen in size and shape, an apparent reversal of the clotting reaction.[133] No specific interaction could be demonstrated between lithium hydroxide and haemoglobin from man, horse and dog.[134] Lithium ions, in common with the alkaline earth metal ions, exert a marked protective action on the deterioration of guinea pig complement at concentrations of 1×10^{-5}M. but accelerate the deterioration at higher concentrations.[135] Antibodies to lithium chloride, which do not however flocculate, have been demonstrated in rabbits.[136] It is found that lithium ions compete with sodium ions but not with potassium ions for transport into the human erythrocyte,[137,138] the ratio between sodium and lithium penetrating being 1·0 to 0·93. A similar competition with sodium has been found to occur in isolated frog skin which has the ability to move lithium against an electrochemical gradient.[139,140]

The initial effect of lithium on neural tissues is largely that of excitation. Thus the respiratory quotient of guinea pig brain is increased, probably owing to an increase in cell permeability,[141] while motor activity is excited in the sensometor cortical centres of the dog.[142] The isolated frog nerve is depolarized by 0·11N. lithium salts, the depolarization being reversible by sodium ions at first but becoming irreversible after 500 minutes.[143,144] The depolarization is delayed at low temperatures, and unlike the effect produced by sodium ions, is preceded by a phase of hyper-polarisation.[145] Lithium resembles sodium in being able to prevent the blocking effect of potassium on nerve conduction.[146] A similar resemblance to sodium is found in the effect on the bioelectric potentials across the protoplasm of *Valonia macrophysa*, the apparent mobilities of the ions in the surface layers being of the same order.[147]

In general lithium lowers the excitability of muscle although the action is complex. The intestine of the chick embryo is stimulated at all stages of development, the action being directly on the muscle and not on the parasympathetic nerves.[148] On the small intestine of the cat and guinea pig increasing concentrations of lithium ions produce first a transitory paralysis, then a brief contraction, and finally a diminution of the peristaltic movements.[149,150] Although this action is similar to that of sodium ions, lithium cannot be substituted for sodium since the excitability is gradually lost in lithium solutions.[151] The order of effectiveness of ions of the alkali metals is not always the same, since lithium is more effective than sodium in causing elongation of the frog stomach muscle[152] but less effective in its action on *Mytilus* muscle.[153] Lithium opposes the contraction of striated muscle caused by veratrine, though less effectively than potassium,[154] while blood vessels become relaxed and hence dilated.[155-158] The irritability of isolated heart muscle is increased by low concentrations of lithium ions[159] while the whole heart is slowed and soon stopped.[160-163] The action of lithium here seems to be antagonistic to that of potassium.[164] The injury potential of smooth muscle is lowered by isotonic concentrations of lithium chloride.[165] The effect on the membrane potential and threshold current for excitation have also been studied.[166,167] The electrocardiograms of animals with a high serum lithium content show marked similarities to those obtained when the serum potassium is high, suggesting that lithium may displace potassium from the cells.[168] Lithium ions have been found to induce rhythmical potential and impedance changes in isolated frog skin[169] when sodium, but not potassium, ions are in contact with the opposite side of the skin. The waves have an amplitude of about 5mV. and a period of three minutes. There have been a few attempts to demonstrate changes in the muscle protein caused by lithium ions.[170-172] The *X*-ray pattern of moist whole frog muscle consists of two rings corresponding to spacings at 4·46 and 9·66A. with signs of orientation in both rings. After treatment with hypertonic concentrations of lithium chloride, the orientation disappears, an additional ring appears at 21·3A. and the outer ring at 9·66A. is split.[170] It is interesting to note that lithium chloride removes the anomalous electrophoretic pattern normally exhibited by the protein, wheat gliadin, a change ascribed to a difference in hydration.[173] The same salt also gave some protection to isolated chromosomes exposed to agents known to produce protein denaturation.[174] No significant changes were evident in the chromosomes of intact cells when treated with lithium salts.[175]

Lithium salts have no appreciable effect on the sense organs of the frog palate,[176] of the eel[177] nor of the aquatic beetle *Laccophilus maculosus,*[178] but are very effective repellants of the termite, *Cryptotermes brevis.*[179]

(*d*) Morphogenetic Effects

A great deal of attention has been devoted to one of the most interesting biological properties of lithium salts which is apparently unique, that of causing abnormalities in developing embryos. Test animals in which the effect has been observed include some twelve species of sea urchin, ascidians amphibians, fish, planarians, pond snails and the fruit fly *Drosophila*. The abnormalities include the development of monsters, which are tailless or headless, with only one eye or none and with concomitant changes in the underlying tissues and structures.[180-185] The abnormalities in *Drosophila* involve the male terminalia and the venation of the wings.[186] Lithium chloride also inhibits the growth of cultures of chicken embryonic heart fibroblasts[187] and of tumour tissue growing in association with chicken embryos and eggs,[188] although the growth of the embryo itself may not be affected. Morphological changes are obtained by treating all stages from the earliest stage of the egg, and susceptibility tends to decline with the stage of development, although there may be a rise in susceptibility at the twenty four cell stage.[189-197] Abnormalities may also be produced by direct injection of lithium chloride solution into the embryo.[198] The effect of temperature appears to depend on the stage at which treatment commences, the number of abnormalities increasing with temperature at an early stage of development but decreasing at later stages.[199] Lithium hinders head regeneration of the worm, *Planaria*, at 3°C. but not at room temperature.[200] Abnormalities appear after treatment with concentrations of the order of 0·0025–0·025M. for one hour[201-206] and have been observed after treatment with 2·4 × 10^{-5}M. for twenty four hours.[207] The first manifestation is an abnormality in the formation of the primitive body cavity (exogastrulation).[208-210] Since the animal pole is suppressed at the expense of the vegetal pole of the embryo, the process is often termed vegetalization.[211,212] Lithium affects only the dorsal-ventral plane of the organism and not its bilateral symmetry.[213] Exogastrulae arise by inhibition of the outermost layer of cells, the ectoderm, rather than of the inner layer or entoderm. The specificity of lithium is thus regarded as residing in its power of localised action on certain specialised regions of the embryo,[209,210] thus causing differential rates of growth, though later stages such as head malformation may be due to interference with the chemical organisers.[214] The action of lithium is intensified by centrifuging the eggs before treatment.[215,216] Lithium salts have a protective action on the ability of the egg to form the fertilization membrane[217] and the element is normally present in this membrane in trace amounts.[218] Lithium also inhibits the animalising action of trypsin on eggs.[219] Lactic acid weakens the morphogenetic effects of lithium in some species but reinforces them in other species.[220] An antagonistic action is shown by calcium ions,[207,221-223] potassium ions,[22,223] cyanide ions,[221,224] sodium azide[225] and pyocyanine.[226,227] There have been attempts to interpret the morphological effects of lithium in terms of the state of hydration of the intracellular proteins[228-233] and salt solutions do in fact produce an increase in the viscosity of the proteins, but the effect is not specific to lithium. Apparently the presence of oxygen is necessary for the production of abnormalities since lithium has no effect on embryos under anaerobic conditions.[234] Both glycolysis and respiration of eggs are reduced by about 20% by lithium ions[235-237] while glycogenesis is increased.[238,239] Certain of the abnormalities have in fact been attributed to a change in the carbohydrate metabolism.[240,241] Treatment with lithium salts causes a change in the content of certain amino acids[242] and an increase in deoxyribose nucleic acid,[243,244] but no change in in the level of homarine.[245] There are marked changes in the activities of certain enzymes[246,247] and it has been suggested that treatment with lithium salts inhibits the development of mitochondria which contain a series of enzymes active in the synthesis of proteins required for development.

(*e*) Toxicity

Lithium was less toxic than potassium to tadpoles[248] and depressed the oxygen consumption of surviving frog skin less than potassium and the alkaline earths.[249] When injected suboccipitally into rabbits lithium chloride was among the least toxic of a series of salts of heavy metals[250] but was markedly toxic by intravenous injection, a rise in blood pressure being produced by as little as 3·3mg.[251] Lithium salts have a paralysing effect on the spinal cord and nervous system.[252,253] There is some evidence of bone lesions caused by stimulation of the osteoblasts.[254] Lithium lactate administered in the food of rats was highly toxic and caused a fall in weight.[255] The toxicity has also been studied on a variety of plant cells, fish, bacteria and isolated mammalian organs.[256] Calculations show that the presence of lithium in tissues is unlikely to increase significantly the radiation dosage arising from the $(n,p)(n,\alpha)$ reaction following exposure to thermal neutrons.[257] Lithium chloride is toxic to human spermatozoa[258,259] and increases the fragility of human red blood cells.[260] There have been a number of cases of lithium poisoning among patients using the salt substitute 'Westsal' (a solution of lithium chloride with citric acid and potassium iodide). Several fatalities have occurred among patients with arteriosclerosis and lithium was regarded as contributing to the cause of death. Patients on a low sodium diet appeared to have increased susceptibility. The symptoms were extreme muscular excitability and irritability, uncontrollable tremors, mental confusion and apathy, blurring of the vision and finally coma. A dose of 4–5g. has given severe symptoms.[261-264] When administered orally to dogs and rats lithium is readily absorbed and distributed uniformly throughout the body water, being excreted almost entirely in the urine. The salt is more toxic and accumulates at a faster rate when the sodium intake is restricted.[265-267] Although lithium salts were formerly used to dissolve uric acid present in the body in certain diseases, it has been shown that it is not possible to attribute any particular solvent properties to these salts,[268] although lithium taurocholate in combination with taurine is stated to be effective for the prevention and dissolution of gall stones.[269] Lithium antimony thiomalate has been proposed as a trypanocide,[270,271] while injections of lithium salts have been employed to treat streptococcal infections.[272] The duration of evipan anæsthesia is increased by administration of lithium salts but there is very little effect on the local action of cocaine and procaine.[273,274]

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CHAPTER II

SODIUM

SECTION XXII

THE OCCURRENCE OF SODIUM

By K. W. ALLEN

No important new sources for the extraction of sodium or its compounds have been discovered since the publication of the original Treatise. Advances have been made largely in the investigation of various minor occurrences and also to a lesser extent in fuller understanding of previously known examples.

Various reviews have appeared giving general information and statistics of the production of sodium salts including borax, salt, and the nitrate, sulphate and carbonate.[1-4]

Perhaps the largest and most important new field has been in the investigations of the occurrence of sodium outside the earth's surface, viz. in the atmosphere, the stratosphere and inter-stellar space and in meteorites, the sun, stars and novæ. Air of the Venetian beach has been found to contain 0·000183 g. of sodium chloride per cubic metre, and the rain falling there from 0·0031 g. to 0·0286 g. per litre of total chloride expressed as sodium chloride.[5]

Studies of sodium occurrence in the stratosphere have depended upon examination of spectra, mainly of twilight and the night sky. Bernard concluded that a layer of excited sodium atoms of terrestrial origin existed at a height of about 60 kilometres.[6-9] Cabannes, Dufay and Gauzit suggested that the layer was at a height of 130 kilometres and arose from meteoric dust of cosmic arigin.[10,11] Later, it was thought that the sodium atoms were emitted from the sun.[12] Vegard and others studied the spectra of auroræ and confirmed the sun as the source of the sodium and further calculated that the layer which contains the sodium atoms extends from a height of 43·7 kilometres to 105·4 kilometres.[13-15] Two recent reviews confirm this generally but indicate heights between 42·5 and 104·5 kilometres.[16,17]

Merrill has made an extended study of the spectra arising from interstellar gas and concludes that this consists of clouds of highly attenuated sodium vapour (and the vapours of some other metals) stretched at irregular intervals between the stars.[18-20] Adams has published a general review of of this problem.[21] Brown and Patterson have examined the analyses of a number of meteorites, and for the silicate phase report an average value of 4·62 ± 0·36 atoms of sodium per 100 atoms of silicon.[22]

The atmosphere of the sun has attracted some careful study and several estimates have been made of the relative abundance of various elements including sodium, which occurs to the extent of approximately one atom per million atoms of all kinds or 0·002% by weight.[23-26]

Neutral atoms of sodium have been detected in some stars,[27,28] while sodium ions have been detected in several others.[29-32] The spectrum of ρ-Cassiopeiæ has shown considerable variation in the amount of emission and absorption due to sodium over the years 1939 to 1947 and it is hoped that this may lead to a better understanding of the formation and dissociation of molecules in the stellar atmospheres.[32]

During their periods of maximum brightness the spectra of many novæ (stars which suddenly increase in brightness and then fade to their original luminosity) have been recorded and studied and in almost all cases the presence of sodium has been reported.[33-38] Nova T Coronæ Borealis, 1946, has been the subject of particular study and all observers comment on the strength of the sodium emission in the early stages of the outburst.[39-41]

Little new information has been published on the mineralogical occurrence of sodium within the earth's crust, and most of such reports have been incidental to some other investigation.

Kundig and de Quervain have reviewed the mineral resources of Switzerland, including the sodium ores.[42] Granitic batholites from Elba (Italy) have been shown to contain 2·67–3·36% of sodium expressed as Na_2O.[43] In the Ural mountains the possibility of using deposits of nepheline, sodalite and other minerals has been explored.[44] In Java, the Muriah volcano yields leucite-tephrites containing up to 3·66% Na_2O.[45] Samples of Kansas salt, used in a spectrographic search for minor elements, contained polyhalite and celestite.[46]

The occurrence of sodium in various natural waters has been investigated by a number of workers. Much of the work has been undertaken with a view to determining the geological origin of the water and for this purpose the results are frequently expressed as a ratio of concentrations of two ions e.g. sodium and potassium.[47-51] Eriksson has collected data on analyses of atmospheric precipitation and has compared the results with those for other natural waters. His work includes a bibliography.[52]

It has been shown that in cultivated plants sodium is present largely as the chloride and is in greatest quantity in the parts of greatest physiological activity.[53] The ash of Brazilian mangroves has been reported as rich in sodium, containing 20% Na.[54]

The sodium content of foods has been investigated. Flour contains 0·003% Na, and bread 0·660% Na;[55] most fruit contains less than 0·01g. per 100g., but tomatoes up to 0·035g. per 100g., while spinach, beet and carrots average 0·05g. per 100g.[56]

In the serum and plasma of blood 90% of the sodium present passes into the filtrate on ultrafiltration; that which remains is equal to the amount fixed in the proteins precipitated by ethyl alcohol.[57]

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SECTION XXIII

THE PREPARATION AND USES OF SODIUM

By J. P. QUIN

THE LABORATORY PREPARATION OF SODIUM

When Mellor wrote the original Treatise metallic sodium, manufactured by the electrolysis of fused sodium hydroxide, was a common article of commerce, and at the present time Downs cell sodium, which attains the remarkably high degree of purity of 99·95%[1] is freely available on the market in the United Kingdom, the United States and many other countries. As might be expected, this material is suitable for all normal laboratory purposes, and it is therefore seldom that the preparation of metallic sodium in the laboratory need be undertaken.

However a number of methods for the formation and preparation of sodium on a small scale have been studied during the last thirty-five years and these are described in the following sub-section. Analytical figures showing the purity of the metal produced by the various methods are given where these are available. Unfortunately in many of the original papers the product is described as 'pure sodium' without the inclusion of any analytical data to justify the description.

In many cases some doubt has arisen as to whether a method of preparation should be dealt with as a laboratory preparation, or would be more appropriately discussed under the heading of manufacture. Much of the work, especially that published in the form of patents, has certainly been done with a view to the ultimate production of metal on the commercial scale. When, however, a method of preparation can be carried out by the use of ordinary laboratory techniques and there is no real evidence that the method has been attempted on the commercial scale, it has been considered for the purposes of this Supplement to rank as a laboratory process. Successful manufacturing processes, and what might be described as technological applications of chemical principles, are on the other hand dealt with under manufacture in a later sub-section (see page 323). It will be appreciated that some borderline cases are bound to occur.

FORMATION AND PREPARATION OF SODIUM BY CHEMICAL PROCESSES

In general it may be said that reactions whereby metallic sodium is produced by chemical processes involve (*a*) the thermal decomposition of sodium salts or (*b*) the thermal reduction of sodium compounds with metallic or non-metallic reducing agents. Since the advent of the electrolytic processes for the manufacture of sodium, however, comparatively little interest has been taken in the thermal production of the metal and, with the notable exception of the investigations of Hackspill and his collaborators, the amount of work carried out in this field in the last few decades has been small.

In an excellent survey of methods for the production of the alkali metals, Hackspill gives the following list of reactions which may be used to produce sodium or any of the alkali metals other than lithium.[2] Hackspill points out that many of the reactions are however of secondary or theoretical importance, and must be considered methods of formation rather than methods of preparation.

$$\begin{aligned}
2MN_3 &= 3N_2 + 2M\\
2MCNO &= 2CO + N_2 + 2M\\
M_3Fe(CN)_6 &= Fe + 3MCN + 3CN\\
2MCN + Fe &= Fe + 2C + N_2 + 2M\\
4MOH + 3Fe &\rightleftharpoons Fe_3O_4 + 2H_2 + 4M\\
2M_2CO_3 + 2Fe &= Fe_2O_3 + CO_2 + CO + 4M\\
2MOH + Al &= MAlO_2 + H_2 + M\\
2MOH + 2Mg &= 2MgO + H_2 + 2M\\
2MCl + Pb &\rightleftharpoons PbCl_2 + 2M\\
2MCl + Ca &\rightleftharpoons CaCl_2 + 2M\\
2MCl + Ba(N_3)_2 &= BaCl_2 + 3N_2 + 2M\\
2MF + Fe &\rightleftharpoons FeF_2 + 2M\\
M_2SO_4 + Fe &\rightleftharpoons FeSO_4 + 2M\\
(2FeSO_4 &= Fe_2O_3 + 2SO_2 + \tfrac{1}{2}O_2)\\
6MOH + 4Fe &\rightleftharpoons 2Fe_2O_3 + 3H_2 + 6M\\
2MAlO_2 + Fe &\rightleftharpoons FeO + Al_2O_3 + 2M
\end{aligned}$$

It is advantageous to work under reduced pressure, when the alkali metal is removed from the sphere of reaction in the gaseous form and condenses in the cooler portion of the apparatus.

It will be noted that in some cases the reaction is reversible. Thus, for example when sodium chloride is heated with iron under reduced pressure, reaction takes place according to the following equation:-

$$Fe + 2NaCl \rightleftharpoons FeCl_2 + 2Na,$$

and a mixture of metallic sodium, sodium chloride, ferrous chloride and iron is recovered from the cooler portion of the apparatus. The ferrous chloride, initially formed by the reduction of the sodium chloride with iron, is in part volatilized along with the sodium and the reverse reaction, whereby ferrous chloride and sodium react to give iron and sodium chloride, then takes place on cooling. If, however, the sodium chloride is replaced by sodium fluoride the ferrous fluoride formed by the reduction is only very slightly volatile and hence remains in the reaction chamber while the sodium metal distils off alone.

The list of reactions given above is not comprehensive, and in particular it is pointed out that a number of other metals can be used in place of iron when carrying out the reduction.

Thermal Decomposition of Sodium Salts.

Sodium is produced by the thermal decomposition of sodium salts such as sodium azide,[3-6] cyanide,[7] cyanate,[8] or ferrocyanide.[9]

Suhrmann and Clusius describe a method whereby sodium can be obtained in a high state of purity by the thermal decomposition of sodium azide.[3] The azide is allowed to decompose slowly by heating it under reduced pressure, not exceeding 0·1 mm. of mercury, over a period of three to four days. To initiate the decomposition it is necessary to attain a temperature of 275°C., but to ensure satisfactory evolution of nitrogen it is desirable to work at 280°C. In these circumstances the liberated sodium metal distils away from any residual mass in the decomposition vessel and may be suitably condensed. The yield of sodium is said to be 100%. It is claimed that the metal so produced is spectrographically pure and in particular is free from traces of gases such as hydrogen, and is therefore suitable for use in investigations on physical properties of sodium. Metal prepared in this way has been used for atomic weight determinations.[5] A possible mechanism of decomposition of sodium azide has been discussed.[6]

The thermal dissociation of sodium cyanide in an atmosphere of (*a*) helium at 600°C., 1000°C. and 1050°C. and (*b*) nitrogen at 1050°C., 1220°C. and 1225°C. has been studied.[7] It is shown that sodium carbide is formed in addition to sodium, carbon and nitrogen. This sodium carbide is turn largely dissociates into carbon and metallic sodium. The partial pressure of sodium at 1050°C. in a helium atmosphere above molten sodium cyanide is 117 mm. of mercury. In nitrogen the partial pressure of sodium over molten sodium cyanide at 1100°C. is 67 mm. When sodium cyanate is heated at 700°C. under reduced pressure decomposition takes place according to the equation:-[8]

$$2NaCNO \rightarrow 2CO + N_2 + 2Na.$$

Little work appears to have been done on the thermal decomposition of sodium ferrocyanide. When a mixture of sodium ferrocyanide and potassium ferrocyanide is heated under reduced pressure a sodium–potassium alloy distils off and forms large silvery drops which remain liquid at room temperature.[9]

Thermal Reduction of Sodium Compounds with Metals and Non-metals.

Little further work has been done on the preparation of sodium by the reduction of sodium compounds with carbon. Pinck has shown on a small laboratory scale that when a mixture of sodium carbonate and graphite is heated at 1000°C. under reduced pressure, a yield of sodium corresponding to 65% of the sodium content of the carbonate is obtained.[10] A number of processes for the manufacture of sodium by this route have been patented, however, and are discussed later (see page 324).

The preparation of sodium by the reduction of sodium chloride with calcium carbide has been studied.[11-17] The reaction, which proceeds according to the equation:-

$$2NaCl + CaC_2 \rightleftharpoons CaCl_2 + 2C + 2Na,$$

is reversible, and it is advantageous to work under reduced pressure or alternatively in a rapid current of inert gas which removes the sodium from the sphere of reaction as vapour. According to Hackspill the reduction proceeds in vacuo at temperatures above 800°C. with a yield of sodium of over 80% estimated on the calcium carbide.[2,11,12]

The reaction has been investigated at temperatures ranging from 600° to 1000°C. under a pressure of 1 mm. mercury [14-16] When the reduction is thus performed using a mixture of approximately 1 mol. of sodium chloride and ½ mol. of calcium carbide, the results shown in Table I (see page 311). are obtained,[15] the yield of sodium being taken as the sodium actually produced, expressed as a percentage of the total metal available in the salt.

The use of excess of calcium carbide has no appreciable effect on the yield of sodium, but when the reduction is carried out under a pressure of 10 mm. of mercury the yield of metal is substantially reduced.

Beneficial effects are obtained by adding up to 10% of calcium fluoride to the reaction mixture of calcium carbide and sodium chloride, but substantially larger amounts of fluoride have an adverse effect on sodium production.[14] The presence of calcium oxide lowers the melting point or softening point of the mixture, but has no other advantage and diminishes the yield of sodium.[14] The product contains over 80% of sodium and less than 0·5% of carbon. The change in free energy ΔG° and the equilibrium constant K of the reaction:-

$$2NaCl + CaC_2 \rightleftharpoons 2Na + CaCl_2 + 2C$$

were calculated as shown below Table I on the next page.

TABLE I. - YIELDS OF SODIUM OBTAINED BY REACTION OF SODIUM CHLORIDE WITH CALCIUM CARBIDE

Time of reaction	Temperature of reaction	% Yield of sodium
½ hr.	700	0·7
	750	6·0
	800	17·2
	850	29·0
	900	35·8
1 hr.	600	-
	650	0·7
	700	2·3
	750	13·9
	800	25·8
	850	44·3
	900	79·0
2 hr.	650	0·9
	700	4·2
	800	45·4
	900	91·7

T°K.	700	800	900	1000	1100
ΔG°	26079	20342	14758	9311	4010
K	$7{\cdot}32 \times 10^{-9}$	$2{\cdot}8 \times 10^{-6}$	$2{\cdot}62 \times 10^{-4}$	$9{\cdot}26 \times 10^{-3}$	$1{\cdot}59 \times 10^{-1}$

T°K.	1200	1300	1400	1500
ΔG°	-1151	-6170	-11051	-15794
K	1·62	$1{\cdot}08 \times 10$	$5{\cdot}29 \times 10$	$1{\cdot}99 \times 10^{2}$

The point of equilibrium where $\Delta G^{\circ} = 0$ is 1180°K. or approximately 900°C. It is claimed that these values agree quite well with the results obtained experimentally.

Russian workers have made a study of the reaction under very similar conditions.[17] They use intimate mixtures of finely ground sodium chloride and calcium carbide briquetted at a pressure of 50 kg. per sq. cm. The sodium chloride is heated for 30 minutes at 600–650° before use, and it is found that an excess of 0·1 mol. of sodium chloride is sufficient to ensure the optimum utilization of the comparatively expensive calcium carbide. When the reduction is carried out under a pressure of 4–5 mm. of mercury, the yield of sodium, calculated on the calcium carbide content of the mixture, reaches a maximum of 44% at 950°C. The ratio (y) of the sodium metal produced to the amount of sodium lost through evaporation of the sodium chloride is 1·0, 0·7–0·8 and 0·5 at 900°C., 950°C. and 1000°C. respectively. The addition of 5% of calcium fluoride or sodium fluoride increased the yield and also the ratio (y); the yield is considerably increased by working under reduced pressure. Thus a mixture containing 6% of sodium fluoride gives a yield of 75–82% under a pressure of 0·5 mm. The authors suggest that the presence of fluoride in the reaction mixture, besides lowering viscosity and so facilitating the reaction, is also beneficial in that it decreases the volatility of the sodium chloride. The sodium metal so obtained is in a more compact form that that obtained by working at higher pressures. The product contains 98·5% of sodium, 0·5% of silicon and up to 1% of iron. It is suggested that the iron content of the material is introduced accidentally when removing the sodium by scraping from the steel tube in which the reaction is carried out.

More recently the reaction has been studied at pressures less than 0·1 mm. of mercury with respect to the effect of temperature, time of heating, molar ratio of sodium chloride to calcium carbide, addition of sodium fluoride, purity of technical calcium carbide, and physical condition of the reaction mixture. It was found that when a mixture of sodium chloride and calcium carbide in the molar ratio 1:2 was heated for 1 hr. under a reduced pressure of 0·1 mm. of mercury, an 89% yield of sodium, based on the calcium carbide used, was obtained. The consumption of 65% calcium carbide was 1·57 g. per g. of sodium.[17a] The reduction of sodium chloride with calcium silicide according to the equation:-

$$2NaCl + CaSi_2 = CaCl_2 + 2Si + 2Na$$

has also been studied under similar conditions, and the effect of temperature, time of heating, molar ratio of sodium chloride to calcium silicide, and addition of calcium fluoride investigated. For 1 hr. at 900°C. with a molar ratio of sodium chloride to calcium silicide of 1:2 the consumption of calcium silicide was 94% and 3·4 g. of silicide was required to produce 1 g. of sodium.[17a]

Industrial processes based on the reduction of sodium compounds with calcium carbide have been proposed and are mentioned later (see page 325).

Sodium cyanide is a reducing agent and sodium may be formed by the reduction of metallic oxides with sodium cyanide in vacuo at temperatures ranging from 560°C., the melting point of sodium cyanide, to 750°C.[8,18] The metallic oxide is reduced to the metal with the simultaneous formation of metallic sodium together with carbon monoxide and nitrogen according to the equation:-

$$2XO + 2NaCN \rightarrow 2X + 2CO + N_2 + 2Na.$$

The secondary reaction:-

$$2CO \rightleftharpoons CO_2 + C,$$

also tends to take place.

When ferric oxide or nickel oxide is reduced with sodium cyanide, liberation of sodium occurs at temperatures approaching 700°C.[8] It frequently happens that alloy formation occurs between the metal produced by the reduction of the metallic oxide and the sodium simultaneously liberated. Thus lead oxide and tin oxide are quantitatively reduced at the melting point of sodium cyanide to yield alloys of sodium with lead and tin respectively. With barium and strontium oxides, reduction proceeds at 750°C. to give alkaline earth metal-sodium alloys. Calcium oxide, alumina and manganese dioxide are reduced by sodium cyanide only with difficulty and the reduction is said to be incomplete.[18]

The formation of sodium by reducing sodium compounds with barium has been discussed.[19] Potassium, caesium or rubidium can be prepared by the thermal reduction of their compounds under reduced pressure with barium, which may conveniently be used in the form of barium azide. Barium azide decomposes between 100° and 200°C. to yield barium metal, which in turn reacts with the compound present to liberate the alkali metal which then distils off as vapour and may be suitably condensed. It is said, however, that owing to the comparatively high distillation temperature of sodium it is difficult to obtain a satisfactory yield of sodium by the barium azide route, and the method is accordingly not recommended for this purpose.

Sodium has been prepared by Hackspill's method whereby sodium compounds such as the chloride are reduced with metallic calcium under low pressure.[2,20,21] At ordinary pressures reduction is incomplete and the metal phase contains both calcium and sodium;[2] it is therefore necessary to separate these metals by distillation, preferably under reduced pressure. If, however, the operation is carried out at a sufficiently low temperature a pure product is obtained. At higher temperatures the metal is found to contain a small amount of calcium which is readily eliminated by a second distillation at 400°C. in glassware under reduced pressure. The preparation of sodium-calcium alloys by the reduction of sodium compounds with calcium is dealt with elsewhere (see pages 315, 325). It is claimed that the method produces very pure sodium which compares favourably with that obtained by other methods of preparation.

A modified form of the Hackspill method dispenses with the use of a high-vacuum pump, and uses a water pump only.[21] The reaction mixture is heated electrically to about 350°C. and when gas evolution ceases, as shown by a fall in the pressure to about 20 mm. of mercury, the water pump is isolated by closing a stopcock or sealing off at a constriction in the connecting tube. The sodium is then distilled off by gradually raising the temperature of the reaction mixture to 800°C. The yield of sodium is only slightly less than that given by the conventional Hackspill method. This modified Hackspill method would appear to provide a simple means of preparing small quantities of metallic sodium in the laboratory without the use of expensive apparatus.

The preparation of sodium by reducing sodium compounds with iron at low pressures and high temperatures has been studied by Hackspill and his collaborators.[2,10,18,22,23] Under reduced pressure the sodium produced is removed from the sphere of reaction as vapour, and it is accordingly possible to work at considerably lower temperatures than when using normal pressures. Thus under such conditions iron displaces sodium from sodium sulphate or arsenate at the melting points of these salts, and from sodium thiocyanate at 650°C.[10,23] Sodium cyanide is completely decomposed when heated with iron at 600°C., whereas sodium borate and metaphosphate require a temperature of 1300-1400°C. before sodium is liberated.[10,23]

In the case of sodium metaphosphate the reaction proceeds according to the equation:-

$$2NaPO_3 + 6Fe \rightarrow 6FeO + 2Na + 2P,$$

and phosphorus is formed in addition to sodium.[10] If, however, the reduction is carried out in the presence of silica, this compound unites with the sodium oxide content of the phosphate to give sodium silicate and in these circumstances only phosphorus and no sodium metal is produced at 1400°C.[10]

Sodium sulphide is reduced by heating with excess of iron in vacuo at about 1000°C. to give an almost quantitative yield of pure sodium metal.[10] This method of preparation has the advantage that it does not produce any volatile product other than metallic sodium. It is claimed that the addition of basic oxides such as calcium oxide to the reaction mixture has a beneficial effect and this has been the subject of a patent.[24] Iron reacts with sodium nitrate in vacuo at 600°C. to give sodium according to the equation:-[10]

$$2NaNO_3 + 4Fe \rightarrow 2Fe_2O_3 + N_2 + 2Na.$$

When sodium halides are heated in vacuo with iron at temperatures above about 800°C., sodium is formed.[10,22] With sodium chloride, bromide and iodide, however, a mixture of ferrous halide and sodium halide distils from the reaction mixture with the sodium vapour.[22] On condensation these halides contaminate the product and the ferrous halide and sodium tend to react to give iron and sodium halide. Sodium and iron fluorides, on the other hand, are much less volatile, and when sodium fluoride reacts with iron in vacuo at temperatures approaching the melting point of the salt, a good yield of sodium is obtained.[22]

Some work has also been done on the decomposition of sodium hydroxide with iron and other metals in a current of nitrogen.[25] Thus when sodium hydroxide and iron are heated at 750°C., metallic sodium distils off and condenses in the cooler portions of the apparatus. At the same time some sodium hydride is formed and this material is likewise volatilized and condensed. When nitrogen containing a little hydrogen is used, only sodium hydride is formed, and as the hydrogen content of the nitrogen is progressively increased, a stage is reached when there is no deposit. It is suggested that in these circumstances the hydrogen reacts with the ferric oxide, initially formed by the reduction of the hydroxide with the iron, and the water so formed reacts in turn with the sodium. This may possibly explain[25] the poor yield given by the Gay Lussac and Thénard process[26] formerly used for the manufacture of sodium.

The reduction of sodium hydroxide with manganese in a current of nitrogen or hydrogen at 600°C. yields sodium, and the reaction proceeds rapidly at 700°C.: at the same time sodium hydride volatilizes and may be condensed in the cooler portions of the apparatus.[25] Ferromanganese and tungsten act in a similar manner, but with chromium a temperature of 800°C. is necessary before sodium is liberated. At 600–700°C. cobalt and nickel appear to produce traces of sodium vapour, but the nickel and cobalt are not oxidized, and no appreciable amount of sodium can be obtained by condensation.

Attempts to prepare sodium by the reduction of sodium hydroxide with zinc in a current of nitrogen or hydrogen were unsuccessful.[25]

Nickel is in general a poor reducing agent for sodium compounds and yields sodium only with sodium hydroxide and sulphide.[10,23]

When a mixture of sodium hydroxide and nickel is heated in vacuo, hydrogen evolution starts about 350°C., and at 600–650°C. metallic sodium is formed and distils off,[10] but the product is contaminated with sodium hydroxide which has been volatilized unchanged. If, however, the sodium hydroxide vapour is passed through a packed tower of powdered nickel at about 650–700°C. it is possible to attain complete reduction, and the product is pure sodium metal.[10]

Nickel does not reduce sodium cyanide, though mixtures of sodium cyanide and nickel heated in vacuo at about 900°C. yield a very small amount of sodium.[10] This is attributed to traces of oxide in the nickel which reacts according to the equation:-

$$2NiO + 2NaCN \rightarrow 2Ni + 2Na + 2CO + N_2.$$

Alternatively it is possible that the sodium cyanide might contain traces of sodium hydroxide. With pure iron-free nickel and pure sodium cyanide no sodium metal is formed.

When sodium sulphide is heated with nickel at about 1000°C. sodium is formed and distils off under reduced pressure,[10] but the yield of metal does not exceed 45%. Oxygen-containing compounds such as sodium carbonate or nitrate do not give sodium when heated with nickel in vacuo. At a sufficiently high temperature sodium oxide is produced and distils over unchanged.[10] Similarly nickel will not reduce sodium halides to form sodium.[10,23]

A disadvantage in reducing sodium compounds such as the chloride with carbon or calcium carbide is the evolution of carbon monoxide. This may be avoided by using, as the reducing agent, silicon or ferrosilicon in the presence of calcium oxide,[27,28] the reaction being:-

$$4NaCl + 4CaO + Si \rightarrow 2CaCl_2 + (2CaO),SiO_2 + 4Na.$$

The reactants, which should be dry, are pulverized, compressed into briquettes, and heated at 850°C. under a pressure not exceeding 250 microns, when the sodium distils off and deposits in a condenser which is preferably heated above the melting point of sodium. It is essential to use about three times the stoicheiometric amount of calcium oxide and 75% yields of sodium have been obtained.[27]

The reduction may also be carried out using an anhydrous sodium silicate in place of sodium chloride[29] at temperatures between 800° and 1300°C., when the sodium distils off and may be recovered by condensation.

The reduction of sodium compounds with potassium does not give sodium but a sodium-potassium alloy and is discussed elsewhere (page 316 and Suppl. 3)

The preparation of sodium may be carried out very conveniently by the thermal reduction of sodium compounds with powdered zirconium metal in vacuo.[30,32,33] The reduction mixture has the advantage of decomposing at not too high a temperature without the formation of any volatile product other than sodium, and the method has been recommended for the preparation of small amounts of sodium in situ for the determination of physical properties of the metal.

Thus a mixture of sodium dichromate and zirconium in the proportion 1:10 reacts smoothly at 250°C. in vacuo with the evolution of sodium.[30] The yield is about 50%, but the metal is contaminated with about 25% of oxide. When sodium chromate is used in place of dichromate the reaction starts about 740°C. and the yield of sodium is about 70%, with an oxide content of 30%.

Better results are obtained with sodium molybdate.[30] When mixtures of this compound and zirconium in the proportions 1:1 or 1:4 are heated in vacuo, the reaction proceeds smoothly at about 550°C., and whereas the 1:1 mixture gives a product containing a small amount of oxide, the 1:4 mixture gives a nearly quantitative yield of pure sodium.

Sodium tungstate likewise reacts readily with zirconium at about 450°C. in vacuo.[30] A 1:1 mixture of tungstate and zirconium gives sodium contaminated with oxide, but a 1:4 mixture gives an 80% yield of sodium free from oxide.

Other reducing agents have been proposed for the reduction of sodium compounds, and the preparation of sodium by reducing sodium sulphide with arsenic or tin[34] and sodium compounds with thorium[31] has been patented. A proposal to use ferrophosphorus as a reducing agent in the production of sodium from sodium carbonate is discussed later (see page 325).

The mechanism of formation of sodium by the reduction of sodium hydroxide with a number of metals including chromium, cobalt, copper, beryllium, tantalum, gold, silver, manganese, iron and ferrous alloys has been studied.[34a]

PREPARATION OF SODIUM ALLOYS BY CHEMICAL REACTION

When molten sodium chloride reacts with metallic calcium, reduction is incomplete and the metal phase produced contains both calcium and sodium. The equilibrium:-

$$2NaCl + Ca \rightleftharpoons CaCl_2 + 2Na$$

has been studied by Lorenz and Winzer who found that the metal phase contains over 99 atomic-% of sodium over wide ranges of temperature and of calcium chloride content in the fused salt phase.[35] Later work by Rinck, however, indicates that, depending on conditions of temperature and concentration of calcium chloride, the metal phase may contain substantial amounts of calcium.[36] By carrying out the reduction in the presence of molten metals such as lead[37,38] or antimony,[37] alloys of these metals with calcium and sodium may be obtained. The equilibrium is discussed in more detail elsewhere (see page 348).

The distribution equilibrium of sodium between molten sodium halides and molten metals such as lead, tin, antimony, cadmium, thallium, bismuth and gold has been studied.[37a]

The reduction of fused sodium compounds such as the hydroxide, fluoride, chloride, bromide or iodide with metallic potassium does not yield pure sodium but a sodium-potassium alloy.[36,39] With molten sodium chloride, the reduction has also been carried out in the presence of lead to give lead-sodium-potassium alloys.[40] The equilibrium in the fused state between potassium, sodium and their halides or hydroxides is discussed in greater detail under Potassium (see Suppl. 3).

The preparation of alloys of sodium with lead[40a] and mercury[40a-d] has been described.

ELECTROLYTIC METHODS OF PREPARATION OF SODIUM

Electrolysis of Aqueous Solutions of Sodium Compounds.

As might be expected, few attempts have been made to prepare sodium by the electrolysis of aqueous solutions of sodium compounds. It is claimed, however, that deposits containing appreciable amounts of free sodium metal have been formed by the electrolysis of sea water under special conditions.[41]

Electrolysis of Solutions of Sodium Salts in Non-aqueous Solvents.

A number of patents have been filed for the preparation of sodium by the electrolysis of solutions of sodium salts in non-aqueous solvents such as liquid ammonia or organic solvents, but there is no indication that such processes have found any technical application, and experimental work appears to have been confined to the laboratory or to comparatively small scale semi-technical operation.

In one process a solution of sodium chloride in liquid ammonia is electrolyzed using a permeable or semipermeable diaphragm and a metallic cathode which does not catalyze the formation of sodamide which tends to take place between the liberated sodium and the solvent, e.g. aluminium, magnesium, cadmium, zinc or tin.[42,43] The anode is of graphite, and the diaphragm of asbestos cloth or porous Alundum. During electrolysis the catholyte, which is an indigo blue solution of sodium in liquid ammonia, is separated from the anolyte and evaporated to give sodium metal. The product may be freed from contaminating sodium chloride by fusion.

Laboratory experiments carried out at Gersthofen, Germany, on the electrolysis of solutions of sodium chloride in liquid ammonia at -10°C. in a wrought iron autoclave which served as cathode, with a cylindrical graphite anode and a diaphragm, yielded sodium heavily contaminated with sodamide.[44] The sodium and the chlorine formed during electrolysis reacted with the solvent as follows:-

$$2Na^+ + 2NH_3 \rightarrow 2NaNH_2 + H_2$$
$$6Cl^- + 8NH_3 \rightarrow 6NH_4Cl + N_2.$$

The evolved gas was a mixture of about 75% of hydrogen and 25% of nitrogen. The efficiency depended on the adoption of a suitable diaphragm. Cotton diaphragms were found to be unsuitable; asbestos cloths and ceramic diaphragms were also tried, and with the latter current efficiencies of up to 80% were obtained in the production of sodamide. It would therefore appear that the process is suitable for producing sodamide rather than metallic sodium.

During the operation of the cell it was found that a considerable increase in voltage took place in the course of a few hours. This was caused by clogging of the diaphragm pores with sodamide, and is most severe when the current density is highest, probably because then the amount of ammonia entering the cathode compartment is no longer sufficient to dissolve the precipitated sodamide. Continuous operation is therefore not possible.

A patent proposes to carry out the electrolysis using a solution of sodium chloride in a solvent mixture of liquid ammonia and an inert organic solvent, in which liquid ammonia is soluble but sodium is substantially insoluble.[45] The organic solvents are selected from a group comprising dioxan, alkyl ethers of molecular weight not exceeding 75, alkyl amines of molecular weight not exceeding 75 and benzene. The organic liquid is present in such amounts that a sodium-rich phase is formed by solution of the alkali metal, produced by electrolysis, in the solvent mixture.

Production of sodium by electrolysis of solutions of anhydrous sodium salts in liquid ammonia and methylamine, ethylamine or pyridine, has also been the subject of a patent.[46,46a] The concentration of the sodium salt in the electrolyte should exceed two molar parts, and the sodium is produced as a colloid, a suspension, a paste, or as a deposited metal, depending on the salt concentration. The electrodes may be of carbon and iron, and the cell operates at current densities ranging from 10 to 100 amp. per sq. dm. Refrigeration is recommended to avoid excessive evaporation of ammonia.

Sodium may also be produced by the electrolysis of a solution of sodium acetylide in liquid ammonia.[47] The sodium so liberated dissolves in the ammonia giving a localized blue colour in the vicinity of the cathode. Small amounts of gas and carbon are produced at the anode. The mechanism of the explosion which occurs after the liberation of sodium during the electrolysis of sodium nitrate in liquid ammonia has been investigated.[47a]

The deposition of sodium from solutions of sodium salts in non-aqueous solvents other than liquid ammonia has also been studied.[48-51]

Work has been reported on the preparation of sodium by the electrolysis of solutions of mixtures of sodium chloride with aluminium chloride or of sodium bromide with aluminium bromide in nitrobenzene and in mixtures of nitrobenzene and xylene.[48,49] With nitrobenzene, a low current density and the use of a diaphragm are recommended.[49] When nitrobenzene and xylene are used, the preferred solvent mixture is one part of xylene to two parts of nitrobenzene, and optimum results are obtained with a current density of 1 amp. per sq. dm., when a solid smooth deposit of sodium with a metallic lustre is obtained. This method of preparation would appear to be applicable to the production of small amounts of sodium in the laboratory.[48]

Attempts to prepare sodium by electrolyzing solutions of sodium iodide or sodium thiocyanate in anhydrous pyridine were unsuccessful.[50]

Electrolytic studies have been made on solutions of sodium chloride, sulphate and nitrate in fused ethylpyridinium bromide, which for this purpose may be regarded as a non-aqueous solvent, although it might with equal propriety be described as a fused salt. All these sodium salts were found to have a very low solubility in ethylpyridinium bromide at about 135°C. and no sodium was obtained by the electrolysis of such solutions.[51]

The electrolytic deposition of sodium from non-aqueous solutions at normal temperatures has been discussed.[51a,b]

Electrolysis of Sodium Compounds in Non-aqueous Solvents Using a Sodium Amalgam Anode.

A novel method for the preparation of sodium was patented by Ewan in 1923,[52,53] by which sodium is obtained by electrolyzing a solution of sodium cyanide in anhydrous liquid ammonia, using a sodium amalgam anode. The operating temperature is maintained between the boiling point and the freezing point of the electrolyte, and the concentration of sodium cyanide in the electrolyte is such that during electrolysis the solution forms two layers: an upper layer, remote from the anode, which contains the sodium, and a lower layer in contact with the amalgam which contains the sodium cyanide in the dissolved state.

The Ewan process has been studied in Germany on the laboratory scale[44] using a two-litre autoclave, and it was found that the voltage seldom exceeded 1·7V. It was also found that when the electrolysis is carried out using an iron cathode, substantial amounts of sodamide are deposited on the cathode as a firmly adhering crust which is very difficult to remove, and that the hydrogen formed contains over 20% of nitrogen. Moreover, small amounts of a highly explosive substance, presumed to be mercury azide, are formed on the anode. These operational difficulties may serve to explain why this interesting process does not appear to have attained any success on the commercial scale.

The preparation of sodium by the electrolysis of solutions of sodium salts in ethylenediamine, using a sodium amalgam anode, has been studied.[44,54-56]

Russian workers electrolyzed solutions of sodium bromide in ethylenediamine at temperatures over 100°C. using a sodium amalgam anode, at current densities varying from 1·4 to 9·0 amp. per sq. dm., but obtained only very small quantities of sodium at low current efficiency.[54] Most of the experimental results are reprinted in an American paper on the subject.[55]

A reinvestigation of the problem by German workers showed that complete dehydration of the ethylenediamine is essential, in order to prevent the formation of sodium hydroxide which is precipitated as a slimy deposit and interferes with efficient electrolysis.[44] To achieve the requisite degree of dryness, it is necessary to rectify the solvent over metallic sodium for several hours, and this results in losses owing to polymerization. In addition considerable polymerization losses occur during the electrolysis, which, it is said, must be carried out near the boiling point of ethylenediamine (116°C.). No efficiency figures are given for the production of sodium in this way.

Better results appear to have been obtained by Putnam and Kobe, who state that it is essential to maintain the operating temperatures at or below the melting point of sodium in order to avoid reaction of that metal with the solvent. In a typical experiment 10 c.c. of a solution containing 25% of potassium iodide and 5% of sodium iodide was electrolyzed in a 20 c.c. test tube, using a 0·5% sodium amalgam anode, a copper cathode of 5 sq. cm. immersed area, and a current of 0·5 amp.; the cell is held at 100°C. during the electrolysis by immersion in a water bath. Pure sodium is said to be liberated at current efficiencies exceeding 90%. No analytical figures for the purity of the sodium are given, however, and in particular the potassium and mercury contents of the metal are not stated. The method appears to offer a convenient laboratory method for the preparation of sodium. A detailed description is given of the method adopted for the purification of the ethylenediamine.[55]

Electrolysis of Fused Sodium Compounds.

The preparation of sodium by the electrolysis of fused sodium hydroxide and fused sodium chloride is discussed in detail elsewhere (see pages 328,332). These processes do not appear to lend themselves to convenient operation on the small scale, and very little information has been published about the laboratory preparation of sodium in this way. A miniature electrolytic cell for the preparation of small quantities of alkali metals has been described. The cell comprises a 1½ × 3 in. graphite crucible into which is inserted a 1 × 3 in. alundum thimble to act as cathode compartment and diaphragm, and a cathode of 3/16 in. stainless steel, and is heated externally. Work on other alkali metals suggests that sodium chloride would provide a suitable electrolyte. The molten metal produced by the electrolysis is withdrawn from the cell by means of a stainless steel pipette.[56a]

The production of sodium by the electrolysis of fused sodium cyanide has, however, been satisfactorily carried out in the laboratory.[57] When fused sodium cyanide is electrolyzed, using a graphite anode and a 1 mm. diameter nickel wire as cathode, sodium is liberated at the cathode in the form of molten drops which rise to the surface of the electrolyte and form a comparatively thick layer above it. The cell operates with a current of 2·5 amp. at 6 V., and sodium is obtained with 90–95% efficiency. Nickel, copper and iron cannot be used for the anode, as these metals dissolve in the fused cyanide. Cyanogen is liberated at the anode during electrolysis, and this may be collected and absorbed in a solution of sodium hydroxide or sodium carbonate, the sodium cyanide so produced being returned to the process at a later stage, after being rendered anhydrous.

The electrolysis of a fused aluminium fluoride–sodium fluoride, AlF_3,-$3NaF$, at 1010°C. with a water-cooled iron cathode gave sodium which contained only a small amount of aluminium. When the cooling is sufficient, it is possible to reduce the amounts of aluminium produced to very small proportions. If a graphite cathode is used, without cooling, then aluminium only is produced.[57a]

It is sometimes found that the sodium formed by the electrolysis of a fused sodium salt enters into secondary reactions with the electrolyte with the result that the product of the electrolysis is not pure sodium but a sodium compound or compounds, which may, however, contain some free metallic sodium.

Thus the preparation of sodium by the electrolysis of fused sodium nitrite has been attempted, but the metal initially formed during the electrolysis enters into a secondary reaction with the electrolyte and the final product is not sodium but sodium compounds.[58] It might be expected that the electrolysis would proceed according to the following equation with the liberation of free sodium, $NaNO_2 \rightarrow Na + NO_2$. Experiments in Pyrex glass apparatus using iron electrodes showed, however, that the sodium liberated at the cathode reacted with the fused nitrite to form sodium monoxide and gaseous nitrogen, while the nitrogen dioxide produced at the anode likewise reacted with the electrolyte to yield sodium nitrate and nitric oxide, and it was only after some time that the concentration of nitrate in the vicinity of the anode became sufficiently high to permit part of the nitrogen dioxide to be liberated from the bath.

Similarly when fused sodium metaphosphate is electrolyzed using a nickel cathode and an iron anode, the sodium produced at the cathode reacts with the fused electrolyte, liberating phosphorus, and forming sodium orthophosphate.[59] At the anode, the following reaction takes place with the formation of phosphorus pentoxide and oxygen: $2PO_3 \rightarrow P_2O_5 + \frac{1}{2}O_2$.

When molten borax is electrolyzed at about 800°C. in a graphite crucible using an internally cooled iron cathode, the metallic deposit on the cathode consists of an inner layer of sodium, a middle layer of sodium and boron, and an outer layer of boron.[60] It is suggested that the sodium produced by the electrolysis tends to react with the fused electrolyte to produce boron, and it is found that increase in the temperature of operation diminishes the yield of sodium and increases the formation of boron. The addition of slightly soluble oxides, such as aluminium oxide or beryllium oxide, is found, however, to prevent reduction of the electrolyte by the sodium almost completely.

A study of the electrolysis of fused systems containing sodium aluminate with cryolite or sodium fluoride has shown that under suitable conditions sodium may be formed.[60a]

Small amounts of highly pure sodium may be prepared by electrolysis through glass.[61-65] When an evacuated glass electric light bulb is partially immersed in a molten sodium compound and a current passes between the filament and an electrode in the molten salt, electrons emitted from the filament are carried to the glass wall and there neutralize sodium ions in the glass, which thus becomes atoms. These are evaporated by the heat and are deposited on the cooler portions of the bulb. Sodium ions from the molten salt replace those of the glass and migrate through it, being in turn neutralized at the inner surface. It is possible under suitable conditions to deposit about 300 mg. of sodium per hour with a 60 W., 110 V. Lamp.[64] Neither potassium nor lithium ions are transported in this way, and the sodium deposited is therefore spectroscopically extremely pure, the potassium present not exceeding 2 p.p.m.[64]

The formation of dendrites of sodium during the electrolysis of glass has been studied.[64a,b]

Theoretical considerations underlying the electrolysis of fused sodium salts have been discussed.[66,67]

Electrolysis of Sodium Compounds in Fused Electrolytes Using a Molten Metal Anode.

The preparation of sodium by the electrolysis of a fused mixture of sodium hydroxide, bromide and iodide, using a molten sodium amalgam anode, has been developed on the technical scale and is discussed under the manufacture of sodium from sodium amalgam. It has been proposed to prepare sodium from a molten alloy of sodium with tin or other metal of similar properties, by electrolyzing a melt consisting chiefly of sodium borate using the molten alloy as anode.[68]

PREPARATION OF SODIUM ALLOYS BY ELECTROLYSIS

The preparation of sodium amalgam by electrolysis of aqueous solutions of sodium chloride in the presence of a new mercury cathode is discussed elsewhere (see Volume II, Supplement 1, pages 299, 307; see also Mellor, IV, 1013). The concentration of sodium amalgam by evaporation of the mercury content is described later (see page 327).

Attempts to prepare substantially pure sodium by the electrolysis of fused mixtures of sodium hydroxide and potassium hydroxide using a sodium amalgam anode were unsatisfactory as the sodium metal so produced contained a considerable amount of potassium, and the method is therefore more suitable for the preparation of a sodium-potassium alloy.[44]

The preparation of metallic sodium in the form of a lead-sodium alloy obtained by electrolyzing molten sodium chloride using a molten lead cathode has been investigated on the laboratory scale in Germany.[69] Electrolysis is carried out at about 850°C. in an extremely heated nickel crucible at 4.5V., using a molten lead cathode in which the liberated sodium dissolves, and a graphite anode at which chlorine is discharged. Alloys containing up to 25–30% of sodium can be prepared with a current efficiency of approximately 100%. At lower temperatures the absorption of sodium in the lead is less complete, and this is attributed to the reduced rate of diffusion of the sodium initially deposited on the surface of the molten cathode. Temperatures higher than 850°C. are inadvisable as the molten salt then shows a tendency to evaporate. Crucibles of porcelain or graphite are rapidly attacked by sodium, and welded iron crucibles tend to leak at the welds. The use of electrolytes containing fluorides, which melt at temperatures down to 500°C., has also been considered. The process has been used on the commercial scale for the manufacture of lead-sodium alloy and is discussed later (see page 353).

Sodium-lead alloys are produced by the electrolysis of a mixture of 7 parts of sodium chloride, 2 parts of sodium fluoride and 1 part of potassium fluoride at 600°C., using a molten lead cathode.

When electrolysis is carried out for 10 hr. at 10–15 V. using a graphite anode, a sodium-lead alloy containing only 0·8% of sodium is obtained at poor current efficiency. Better results are obtained when potassium bifluoride or ammonium bifluoride was substituted for potassium fluoride in the melt, and in these circumstances it proved possible to obtain alloys containing 2% of sodium.[69a]

Lead-sodium-potassium alloys have been prepared by the electrolysis of a fused mixture of sodium and potassium chlorides using a molten lead cathode.[70] Ternary alloys of sodium and barium with tin, antimony and bismuth have been prepared by electrolyzing fused mixtures of sodium and barium chlorides with a molten metal cathode of tin, antimony or bismuth[71] and ternary alloys of sodium and calcium with antimony and bismuth have been similarly obtained from fused mixtures of sodium and calcium chlorides.[71]

Sodium has been isolated in the form of a sodium-lead alloy by the electrolysis of molten sodium cyanide, with or without sodium halides, using a lead cathode and a carbon anode.[71a] A sodium-mercury alloy has been prepared by electrolysis of a fused melt containing 46% of sodium hydroxide, 27% of sodium bromide, 18% of sodium iodide and 9% of sodium cyanide in the presence of a mercury cathode at 280°C. Glass vessels are rapidly attacked by the melt but sintered alumina is satisfactory.[71a]

The preparation of sodium-calcium alloys in the Downs cell is described later (see page 340).

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THE MANUFACTURE OF SODIUM

Sodium was originally manufactured by reducing sodium compounds with suitable reducing agents at high temperatures, but in 1890 Castner applied for a patent for producing the metal by electrolysis of fused sodium hydroxide and by 1893 was making sodium on the commercial scale at Oldbury, England, at the rate of about two tons per week.[1]

The ease and simplicity of the Castner process offered very considerable advantages over the older high temperature processes, which consequently become obsolete in a very short time. The Castner cell rapidly attained considerable commercial success and as such, or in a slightly modified form, was soon operating in Germany, Norway, Italy, France, Japan and the United States.[2]

Until the middle of the nineteen twenties the Castner process was to all intents and purposes the only practical method of manufacturing sodium, and in 1926 the world production of sodium by this means reached a peak of 15,000 tons. This was before the use of sodium in the manufacture of tetraethyl lead caused a considerable rise in world production.[3]

However, about this time the Downs process for the manufacture of sodium by the electrolysis of fused sodium chloride was successfully developed in the United States and since then the Castner process has been gradually superseded. Castner cell sodium is no longer made in England or the United States, but a Castner process was working in France up to 1940 and the cell was still in operation in Japan in 1954.[3] In 1944 the German Castner capacity was 160 metric tons per month.[4]

The Castner process is now unlikely to be established in a new works unless the required quantity of sodium must be made 'on the spot' and is insufficient to warrant the erection of Downs cells which have a comparatively large output.[3]

In the United Kingdom the first Downs plant was installed in 1937, and since then other plants have come into operation. Before the second world war there were two producers in Germany.[2] Degussa operated Downs cells with a total capacity of 650 metric tons per month, and I. G. Farbenindustrie used Castner cells having a total capacity of 80 metric tons per month but operated at a low output.[4]

The following estimated outputs of sodium are given for 1954:-[2]

	Tons per Annum
Western Germany	8,000
France	3,000
Italy	No figures available
Japan	2,500

The total capacity of the sodium plants in the United States in 1954 was approximately 300 million pounds per year, and the output of sodium in 1952 was 123,187 tons and in 1953 120,481 tons.[5]

The following figures given for the estimated world production of sodium illustrate the growth of the demand for the metal.[2]

Year	Estimated World Production Tons	Castner	Downs
		% of total output	
1900	1000-2000	100	-
1910	11,000	100	-
1920	12,500	100	-
1930	18,000-20,000	50	50
1940	73,000	15	85
1952	140,000	5	95

In an estimate published in 1957 the world production of sodium is given as about 300 million lb. annually, about 260 million lb. of this being produced in the United States. The largest American producer is the Ethyl Corporation with plants at Baton Rouge, Louisiana, and Pasadena, Texas. The second largest producer is Du Pont with a plant at Niagara Falls, N. York, and a second plant scheduled to go into production at Antioch, California, in 1957. The third largest producer is National Distillers Products Corp. with a plant at Astabula, Ohio, built in 1951 and now being expanded. The repective capacities of these three producers are about 120, 100 and 40 million lb. of sodium per year.[6a]

Small tonnages of sodium have also been made by other processes. Thus, for example, the Ciba process[6,7] which operates in Switzerland was producing 500 tons per year in 1926.[7] No recent figures appear to be available for Ciba cell production however. A number of reviews describing the development of the manufacture of sodium metal give more detailed information on this subject and some have extensive bibliographies.[1-3,8-15c]

THE MANUFACTURE OF SODIUM BY THERMAL PROCESSES

No evidence has been found that the manufacture of sodium has been carried out by thermal reduction on any significant scale during the last thirty five years. The metal was at one time made by reducing sodium compounds with carbon, but the successful development of the electrolytic routes to the metal rendered all other methods of production obsolete. It is, however, possible that the manufacture of sodium by chemical means may still prove attractive in localities where it is essential that the metal is made on the spot and where no electrical power supply is available.[3] It has in fact been suggested that an improved Deville method of manufacture, whereby sodium is distilled from a fused mixture of sodium carbonate and carbon, could produce cheaper sodium than an electrolytic process,[16] and in recent years a number of patents covering thermal routes to the metal testify to a continued interest in this subject.

Thus, patents have been granted for processes for sodium manufacture involving the reduction of sodium compounds such as the carbonate or hydroxide[17-20] or borax[21] with carbon. In the former case the reduction may be carried out under reduced pressure,[18-20] while in the latter sodium is evolved at a temperature of 1000-1200°C., and is recovered by condensation, followed by sublimation of boric oxide at 1300-1400°C. A recent patent describes a process whereby molten sodium hydroxide reacts with carbon at 800-950°C. while a stream of hydrogen or inert gas is passed through the mixture. Hydrogen is the preferred gas as it gives the best yield of sodium (approx. 85%). The gas pressure is approximately atmospheric and the amount of sweeping gas is about 4-5 times the amount of hydrogen formed by the reaction:-[20a]

$$6NaOH + 2C = 2Na + 3H_2 + 2Na_2CO_3.$$

In one method of manufacture, sodium carbonate is reduced with carbon in a high-temperature reactor to produce sodium vapour and carbon monoxide. The sodium vapour is condensed to give liquid sodium and a dross consisting of sodium carbonate and carbon. The sodium is separated from the dross by fluxing with sodium hydroxide. The flux is then contacted with carbon monoxide at a temperature of at least 318°C. when sodium carbonate is produced. The treated flux is then recycled to the reactor.[20b] Patents have also been granted for a method of producing sodium metal in which sodium chloride or sulphate is mixed with a non-volatile base such as calcium oxide and a reducing agent such as coke, and then heated in an induction furnace under reduced pressure in an inert atmosphere to a temperature at which the liberated sodium distils off, and may be recovered by condensation.[22-25]

Some attention has been directed towards the development of thermal processes, in which the sodium vapour produced is rapidly condensed and removed from the admixed gases, such as carbon monoxide, formed as by-products during the reduction.

In one such process the carbon monoxide and sodium vapour mixture, produced by reducing sodium carbonate with carbon, is diluted with a cooling gas such as carbon monoxide in order to condense the sodium as liquid metal.[26] In another process a mixture of sodium carbonate and carbon is introduced into a furnace at 1200°C., or above, at a pressure of 0·5 atm.[27] The mixture of sodium vapour and carbon monoxide evolved is expanded to a reduced pressure of 0·4–4 mm. of mercury, and rapidly chilled at 375–400°C. by means of a quenching liquid which is a sodium-lead alloy containing 5–15% of sodium. Part of the quenching liquid is withdrawn continuously into a still at a temperature of 600°C. whence the sodium is recovered by distillation, presumably at reduced pressure. Other quenching liquids, such as volatile metals miscible with sodium, molten salt mixtures and heavy oils, may also be used. It is claimed that this method of preparation produces sodium at good efficiency with a high rate of working.

Another patented process recovers sodium from gases containing sodium vapour by absorbing the metal in molten tin at temperatures varying between 900°C. and 1200°C.[28, 28a]

A patent has been granted for a process in which sodium vapour produced by reducing sodium carbonate with carbon at 1100°–1200°C. is condensed by molten sodium metal at 110°–150°C. Molten lead can also be used as a cooling liquid and in these circumstances a sodium-lead alloy containing up to 28% of sodium may be obtained.[29]

A number of patents relate to proposed processes in which sodium chloride is reduced with calcium carbide.[30-34] The reaction may be carried out under reduced pressure,[31, 32] or in a current of inert gas.[33] The use of a cooling gas to promote condensation of the vapour to liquid metal has been proposed.[34]

Sodium may also be prepared from sodium chloride by passing the vaporized chloride through a heated zone at a temperature between 800–1100°C. containing solid calcium carbide, at a pressure substantially less than atmospheric, whereby the sodium chloride is reduced and metallic sodium vapour produced. The sodium vapour is then condensed and recovered.[33a,b]

Ferrophosphorus has also been proposed as a reducing agent for sodium carbonate or hydroxide. A caked or briquetted mixture of finely ground ferrophosphorus and the sodium compound is heated at 900°–1500°C. under reduced pressure, and the gaseous products quickly removed from the reaction vessel and rapidly cooled to separate the sodium metal from the other gaseous products. Condensation of the sodium may be brought about by introducing a spray of cooled mineral oil.[35] The reduction of sodium chloride with silicon in the presence of lime has been tried out on a comparatively large scale and a 2000 lb. batch has been reduced in 24 hr. giving a 75% yield of sodium.[36]

The manufacture of sodium by reduction of sodium aluminate with metallic aluminium at a temperature above the melting point but below the boiling point of aluminium has been patented.[36c]

The reduction of sodium ferrite[36a] and sodium silicate[36b] with iron has been the subject of patents.

THE MANUFACTURE OF SODIUM ALLOYS BY THERMAL MEANS

The preparation of sodium alloys by thermal means has been the subject of a number of patents.[37-40]

A metal compound other than an alkali metal compound, e.g. a mercury or lead salt, is treated with a solution of an alkali metal addition compound of an organic compound, such as a sodium naphthalene addition compound, to effect production of a sodium–lead alloy or a sodium–mercury alloy.[38]

Sodium–lead alloys are produced by heating sodium and lead to form a molten mass which is protected by a flux of 3 parts of potassium hydroxide and 2 parts of sodium hydroxide or other material which will not contaminate the alloy.[39]

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MANUFACTURE OF SODIUM FROM MERCURY CELL AMALGAM

Sodium amalgam produced by the electrolysis of brine in a mercury type cell represents a cheap potential source of sodium metal, and it is therefore not surprising that some attention has been directed towards the utilization of brine cell amalgam as a raw material for the manufacture of sodium.

Sodium is in fact obtained very simply from sodium amalgam by the removal of the mercury content of the amalgam by distillation, and as long ago as 1903 an apparatus was patented for carrying out this process continuously.[1] The amalgam was tapped from a brine cell, distilled to leave a residue of metallic sodium, and the vaporized mercury returned to the cell after condensation for further enrichment by electrolysis. The preparation of sodium in this way suffers from the serious disadvantage that the sodium content of brine cell amalgam is low and the weight of mercury which has to be evaporated per unit weight of sodium is therefore very large indeed.

In order to avoid this it has been proposed to operate a mercury cell at a sodium concentration in the amalgam sufficiently high to permit the recovery of a solid alloy, $NaHg_3$, on cooling the amalgam. Thus by operating at a temperature above 70°C. the sodium content of the amalgam may be permitted to rise to 1%, which corresponds to its solubility at this temperature. On cooling to 0°C., where the solubility is about 0·5%, about half the sodium can be recovered by filtering out the solid crystals of $NaHg_3$. The filtrate is then reheated and recycled to the electrolysis cell. Metallic sodium is recovered from the $NaHg_3$ by distilling off the mercury in a retort. It has been pointed out, however, that when the sodium concentration in the amalgam is allowed to exceed about 0·2 to 0·3%, the current efficiency of the mercury cell falls off, hydrogen is evolved in dangerous amounts along with the chlorine, and other difficulties in cell operation are encountered.[2]

A process has been patented whereby sodium is prepared from amalgam without the necessity of operating the mercury cell at high sodium concentrations.[2-5c] In order to ensure optimum electrolytic operation the mercury cell is run at the usual amalgam concentration of about 0·2% of sodium. This amalgam is then withdrawn from the cell and concentrated to about 0·34% of sodium in a multi-effect evaporator using mercury vapour as a heating medium. The partially concentrated amalgam is then concentrated to about 50% of sodium in a mercury boiler. It will be noted that the melting point of 50% sodium amalgam is approximately 42°C. It is claimed that by operating the boiler on a continuous basis it is possible to avoid the formation of the high-melting intermediate amalgams, such as $NaHg_2$ with a melting point of 354°C. The 50% sodium amalgam is then distilled in a retort to give metallic sodium, and mercury which is recycled. It should be remarked that sodium made from amalgam contains small amounts of mercury as an impurity.

Recent patents[6-6b] propose to recover sodium from sodium amalgam by first increasing the sodium content of the amalgam to 10% and preferably to 40–60% by weight, by distillation. The concentrated amalgam is then treated with solvents such as liquid ammonia, ethylenediamine, methylamine or fused sodium hydroxide. Thus sodium may be extracted from concentrated amalgam by treatment with fused sodium hydroxide at temperatures between 325° and 600°C., and by the addition of substances such as sodium carbonate, potassium hydroxide, sodium bromide or sodium iodide, the minimum temperature may be reduced below 325°C. Extraction of the sodium from the concentrated amalgam is simplified by the inversion of the two liquid layers, the concentrated amalgam floating on the fused hydroxide and sinking below it as denudation proceeds. It is said that the sodium may be recovered from the hydroxide solution by raising its temperature (see page 335).

ELECTROLYSIS OF FUSED SODIUM COMPOUNDS USING AN AMALGAM ANODE

The Gilbert Process.

The production of metallic sodium by the electrolysis of a solution of a sodium salt in anhydrous liquid ammonia using a liquid sodium amalgam anode, as proposed by Ewan,[7] does not appear to have been operated on the commercial scale, but a process devised in America by Gilbert on somewhat analogous lines seems to have been more successful and has reached the pilot plant scale.[8-18]

In the Gilbert process sodium is prepared by the electrolysis of fused sodium hydroxide, which may or may not contain other sodium salts, in the presence of a liquid sodium amalgam anode. Little information is available as to the development of the process in America. In Germany, however, the process was developed by the I. G. Farbenindustrie immediately prior to, and also during, the 1939–45 war, and a considerable amount of information has been published on the design and operation of a pilot plant at Gersthofen, near Augsburg.[18] This plant consisted of a 1000 amp. cell having revolving metal discs which picked up a thin film of sodium amalgam, and so acted as the anode. The cell, shown diagrammatically in Fig. 1, operates at low voltage and good current efficiency. A brief description of the design and operation is given below. Table II gives a summary of the design and operating data for the 1000 amp. cell and also for a proposed 16,000 amp. cell.[18]

The cell has four principal parts, viz. the lower, middle and upper sections, and a rotor. The lower section is a semi-circular well containing the rotor, consisting of three nickel discs carried by a shaft entering the well through a combined packing gland and bearing on one side, and supported by a bearing block on the opposite side. The packing is graphitized asbestos and oil. Two cast iron displacers fitted between the discs reduce the mercury capacity of the cell. The amalgam enters through an inlet pipe and amalgam trap at one side of the cell, and leaves through a similar trap and outlet pipe at the opposite side of the cell. Anode bus bars are fitted to the section and the well has a jacket through which heated oil is circulated to maintain a temperature of 230–250°C.

The middle section serves as insulation between the cathodic top section

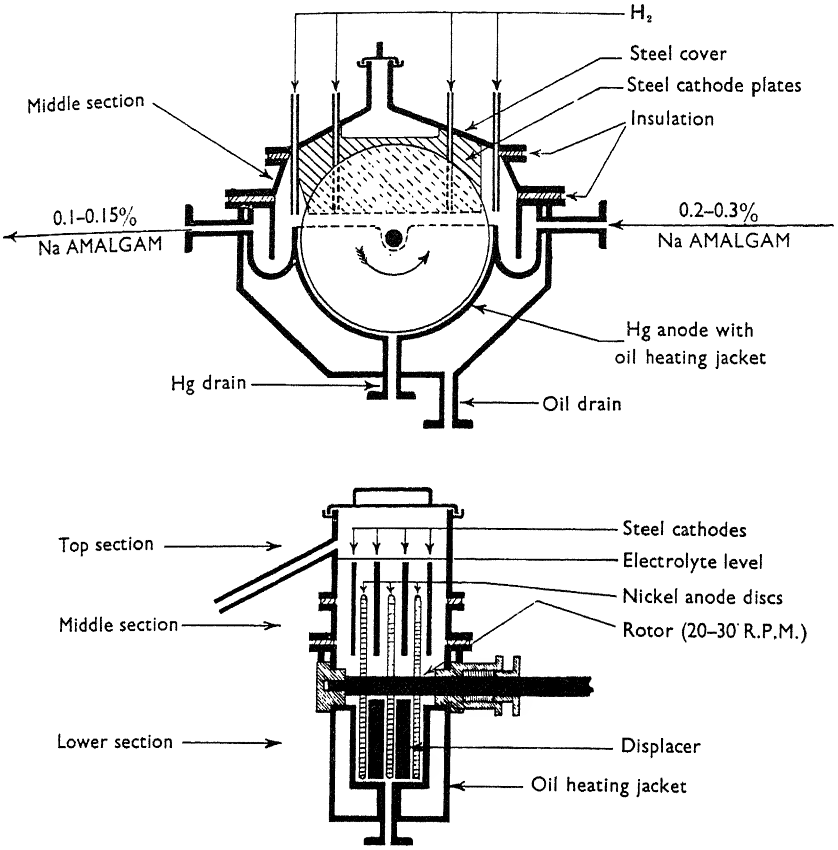
H2
Steel cover
Steel cathode plates
Insulation
Middle section
0.1–0.15%
Na AMALGAM
0.2–0.3%
Na AMALGAM
Hg anode with
oil heating jacket
Hg drain
Oil drain
Top section
Middle section
Lower section
Steel cathodes
Electrolyte level
Nickel anode discs
Rotor (20–30 R.P.M.)
Displacer
Oil heating jacket

FIG. 1. I. G. FARBENINDUSTRIE 1000 AMP. EXPERIMENTAL VERTICAL SODIUM CELL

and the anodic lower section. The top section carries the nickel cathode connexions, two pipes for introducing hydrogen into the melt, an overflow for the sodium metal and a readily removable cover. There are two cathodes centred between the three anode discs, and two cathodes on the outer side of the two outer anode discs.

The cell is filled with a molten mixture of 53% of sodium hydroxide, 28% of sodium bromide and 19% of sodium iodide: this electrolyte can be used at temperatures down to 230°C.[17] The cell is run in conjunction with a mercury-type chlorine cell the amalgam from which is pumped to a constant head tank, where the stream is divided into two parts, one going to the sodium cell, and the other to the amalgam denuder of the chlorine cell. The amalgam stream to the sodium cell, preheated in a heat exchanger by means of the semi-denuded amalgam returning from the sodium cell,[18] is then further heated to 250°C. The amalgam is passed through the cell at such a rate that the sodium concentration on entering and leaving the cell is 0·2–0·3% and 0·1–0·15% respectively, so that it is denuded of only about one half of its sodium content, after which it is returned to the chlorine cell denuder where the residual sodium is decomposed with water to give a ·50% sodium hydroxide. It is desirable to introduce the amalgam near the surface of the pool of amal-

TABLE II. - OPERATING DATA FOR THE GERSTHOFEN SODIUM AMALGAM CELLS

	1000 amp. cell	16,000 amp. cell
Daily production of sodium (85% efficiency)	18 kg.	285 kg.
% Sodium in amalgam entering sodium cell	0·2–0·3	0·2–0·3
% Sodium in amalgam leaving sodium cell	0·1–0·15	0·1–0·15
% Mercury in sodium metal	0·5–1·0	0·5–1·0
% Mercury in purified sodium	0·01	0·01
Calcium used for purification per 100 kg. sodium, kg.	0·6	0·6
Hydrogen used m^3/cell/day	0·7–1·5	0·5–1·0
Cell operating temperature	230–250° C.	230–250° C.
Temperature of purification of sodium	380° C.	380° C.
Cell voltage	1·5–1·9 volts	1·5–1·9 volts
Current efficiency	80–90%	80–90%
Length of sodium cell	900 mm.	2020 mm.
Width of sodium cell	700 mm.	1645 mm.
Height of sodium cell	980 mm.	1790 mm.
Nickel Anode Discs:		
Number	3	11
Diameter	600 mm.	1000 mm.
Thickness	5 mm.	15 mm.
Area	0·85 m^2	10·6 m^2
Current density	1660 amp./m^2	1500 amp./m^2
Revs. per minute	20–30	20–30
Drum diameter	50 mm.	300 mm.
Steel Cathodes:		
Number	4	12
Thickness	5 and 10 mm.	10 mm.
Active area	0·85 m^2	9·5 m^2
Current density	1660 amp./m^2	1700 amp./m^2
Anode to cathode, distance	15 mm.	15 mm.
Cast iron displacers, thickness	30 mm.	30 mm.
Displacers to discs, distance	5 mm.	5 mm.

gam in the cell rather than at the bottom. The electrolysis is carried out under a protective atmosphere of hydrogen.

Adequate amalgamation of the nickel discs is ensured by rotating them at 20–30 revolutions per minute in such a direction that the disc surfaces leave the amalgam at the point where the sodium concentration is highest. At higher speeds of rotation mercury loss tends to become excessive and the efficiency of sodium production diminishes. Nickel discs are superior to steel as the amalgam adheres more readily to nickel, and this permits the use of higher current densities. Current densities up to 3800 amp. per sq. m. can be used with monel and copper discs, but these materials corrode considerably more than nickel. The sodium in the amalgam dissolves in the melt and on electrolysis is deposited on the cathodes. The metal is molten at the temperature of operation and hence floats to the surface of the electrolyte where it is tapped off via the overflow pipe. On a small output the sodium tends to become viscous owing to the presence of sodium oxide and in these circumstances the metal may be removed by bailing.

During operation, hydrogen is bubbled through the melt from each hydrogen pipe. Reaction between the sodium hydroxide and sodium occurs to a small extent:-

$$NaOH + 2Na \rightarrow Na_2O + NaH.$$

The sodium hydride is said to be soluble in metallic sodium and to be thus removed from the cell. The sodium oxide forms a mud, however, which is reduced by the hydrogen. Sodium oxide may also be formed by ingress of air into the system. The reduction of sodium oxide by hydrogen is said to result in a slow build up of sodium hydroxide in the bath, so that sodium bromide and iodide must be added in the correct proportions every two days in order to keep the composition of the electrolyte constant. To keep the level of the bath constant it is of course necessary to remove some of the electrolyte from time to time. Sodium carbonate, which may be formed by contact of the melt with carbon dioxide from the air, appears to have a limited solubility in the electrolyte and may produce a sludge containing substantial amounts of carbonate. Originally nitrogen was used as the protective gas, but this was changed to hydrogen with beneficial results.[18]

The decomposition potential of the cell is given as 0·85 V. The cell voltage starts at 1·5 V. but rises to about 1·9 V. after about 120 days. This is accompanied by a drop in current efficiency from 95% to 85–90% and is taken as an indication that the cell has reached the end of its useful life. No trouble is experienced from carry over of sodium chloride with the amalgam, and the sodium chloride content of the electrolyte never exceeds 0·5%.[18]

The electrolyte freezes at about 220°C. and it is desirable to work as near to this temperature as possible in order to reduce contamination of the sodium with mercury. It is said that a further lowering of the melting point of sodium hydroxide through further additions of sodium halides is theoretically possible. This would offer the advantage of a smaller temperature difference between the chlorine and the sodium cells, and would also decrease the mercury content of the sodium, since this is attributed primarily to the vapour pressure of mercury.[16]

The use of an electrolyte of pure sodium hydroxide is unsatisfactory, because it is then necessary to work at temperatures above 300°C., and the considerable amount of mercury taken up by the melt disturbs the smooth operation of the electrolysis. Trouble is also experienced owing to fog formation in the electrolyte, which makes it difficult to deposit the liberated sodium in a coherent metal phase.[16]

The sodium bromide and iodide content of the electrolyte removed from the cells from time to time during operation, and at the end of the life of a cell, is recovered by recrystallization from aqueous solution. No figures are given, however, for the loss of sodium bromide and iodide occurring during cell operation.[18]

The sodium metal produced by the cell contains 0·5–1·0% of mercury, which renders the sodium hard and unusable, and also represents a serious loss of mercury. By passing the molten metal over calcium at 380°C., the mercury content of the sodium may be reduced to about 0·01%, but this is still appreciable and for some purposes may be deleterious. The calcium consumption is 0·6 to 1·0 kg. per 100 kg. of sodium. Mercury is recovered from the calcium by retorting, after which the calcium residue may be used for a further treatment. Mercury is also recovered by cooling the hydrogen which leaves the cell.[18]

It is said that the hazard from mercury poisoning in the process is no more serious than that when using ordinary mercury-type chlorine cells. Admittedly the operating temperature is considerably higher in the former case, but on the other hand the operations are carried out in an enclosed system.[18]

The following figures are given for the energy requirements of the amalgam route. The d.c. energy required for the recovery of the sodium by electrolysis of the amalgam is approximately 2·75 kWh. per kg. of sodium.[18] The total d.c. energy required, including the production of sodium amalgam by aqueous electrolysis, is estimated to be 9·85 kWh. per kg. of sodium.[2] Another estimate gives a figure of 10 kWh. for the d.c. energy required for the electrolytic production of 1 kg. of sodium by the amalgam route.[18] A comparison of the economics of the Downs cell and the sodium amalgam routes to sodium metal has been made on the basis of pilot plant data obtained at Gersthofen. This suggests that sodium from the amalgam route may be cheaper than that manufactured by the Downs Cell.[18,19] The design of a 16,000 amp. cell has been described, but apparently this cell has not actually operated.

Technical and economic aspects of the electrolysis of sodium amalgam as an anode using a molten electrolyte of sodium hydroxide, bromide or iodide have been reviewed.[19a]

The production of metallic sodium from sodium amalgam has been studied by Japanese workers.[20-23] The densities and electrical conductivities of fused sodium hydroxide, sodium bromide and sodium iodide systems have been determined.[21] The solubility of metallic sodium and other materials in molten mixtures of sodium hydroxide, sodium bromide and sodium iodide has also been determined.[22,23]

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ELECTROLYSIS OF FUSED SODIUM HYDROXIDE

The most successful cell developed for the electrolysis of fused sodium hydroxide is the Castner cell.[1,2,3] Mellor has described the type of cell in operation when the original Treatise was written (Mellor,II,6) and an excellent account of the design and operation of a modern Castner cell, which was in service at Wallsend, England, till 1952, has been given by Wallace.[1]

The Wallsend Castner cell, shown diagrammatically in Fig. 2, is a cast iron pot set in brickwork. A cylindrical anode of pure nickel, made from fabricated plate, rests on a cast iron ring which in turn rests on the rim of the pot, and is insulated therefrom by asbestos board insertions. The cathode is of pure copper and consists of a cylindrical head carried by a stem. The bottom of the pot has an extended base pipe in which the cathode stem is centred and sealed in position by filling the pipe with molten electrolyte which is then allowed to solidify. The electrodes are located 1 in. apart and half way between them is an iron wire gauze diaphragm which permits free circulation of the electrolyte but prevents the globules of sodium reaching the anode. This diaphragm is suspended from a steel cylinder or inner pot resting in a recess in the top ring of the anode, from which it is insulated by asbestos, and extends downwards to the top of the anode: the attached diaphragm extends downwards to the full length of the cathode head. The inner

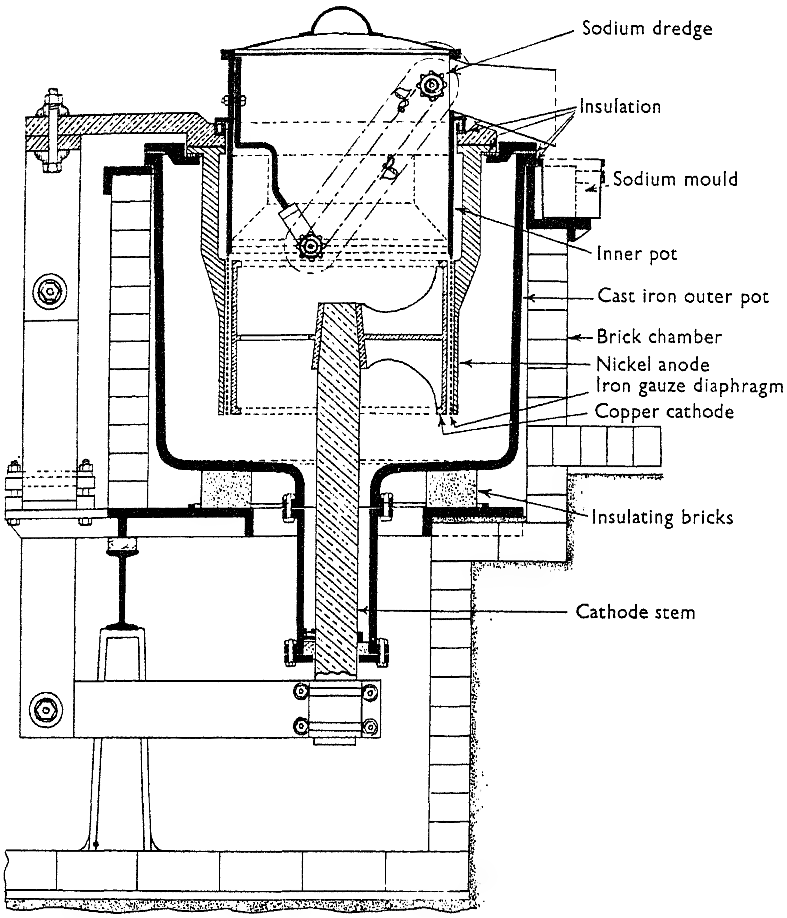
Sodium dredge
Insulation
Sodium mould
Inner pot
Cast iron outer pot
Brick chamber
Nickel anode
Iron gauze diaphragm
Copper cathode
Insulating bricks
Cathode stem

FIG. 2. CASTNER SODIUM CELL

cylinder is also fitted with a steel cover which fits closely enough to maintain an atmosphere of hydrogen in the pot, thus avoiding oxidation of the sodium collected there. The oxygen liberated at the anode leaves the cell by a vent from the space outside the cylinder. During electrolysis the sodium deposited on the cathode rises through the denser electrolyte and accumulates in the inner pot whence it is removed by means of a mechanically operated bucket elevator having iron wire gauze buckets. These buckets permit the electrolyte to drain from the mixture of sodium and electrolyte which they lift from the cell, but retain the molten metal. At the turn of its travel the bucket deposits the sodium in a small compartment whence the metal discharges into a mould. Make-up sodium hydroxide is fed into the anode compartment through an opening in the cell cover.

The cell, which has an internal diameter of 39 in. and measures 54 in. from the top to the bottom of the base pipe, holds about a ton of electrolyte. No external heating is applied to the cell, the current being sufficient to maintain the electrolyte in the molten condition.

The process yields sodium and hydrogen at the cathode and oxygen at the anode. It is not considered possible to collect the hydrogen, and although by the exercise of considerable ingenuity the oxygen has been recovered, this does not seem to be an economic proposition.

The cell bath consists of fused mercury cell sodium hydroxide with 10% of sodium chloride and 5–10% of sodium carbonate, and the working temperature is 300–310°C. It is essential to keep this temperature as near the melting point of the electrolyte as is practicable; otherwise the efficiency of sodium production falls off. The usage of sodium hydroxide is 2 pounds per pound of sodium or, allowing for sodium hydroxide recovered by aqueous leaching, 1·8–1·81 pounds per pound of sodium.

The sodium hydroxide fed to the cell contains small quantities of sulphate, calcium and silica, as may be seen from the analysis given in Table III (see page 337). These impurities tend to accumulate in the electrolyte as the bath grows older, and after about 70 days the efficiency falls off and it becomes necessary to shut down the cell. At this stage the electrolyte contains about 20% of sodium chloride, 15% of carbonate, 0·3% of silica, and 0·2–0·3% of sulphate, together with iron oxides in suspension. After the current has been shut off, the electrolyte is pumped out and allowed to solidify. The solidified electrolyte is then broken up and the caustic content recovered by aqueous leaching. The cell assembly is cleaned by washing with water.

It is interesting to note that aluminium makes a very good cathode and is not appreciably attacked by molten sodium or sodium hydroxide. It cannot be used in practice, however, as it will nót resist the strong hot aqueous sodium hydroxide solution formed when the cell is being cleaned after dismantling, as described later. On the other hand it was found that aluminium is of no use as an anode: the current passes momentarily and then falls to zero, presumably owing to the formation of a film of oxide on the metal.

The cells are operated in series with a current of 8500–9500 amp. giving a cathode current density of approximately 7 amp. per sq. in. The yield of sodium is 0·4 g. per amp. hr. and 90 g. per kWh.[1] If the decomposition potential of sodium hydroxide is taken as 2·25 V. at the temperature of cell operation, and the cell current efficiency is 40%, then the energy efficiency can be calculated to be 18%.[476]

Little seems to have been published regarding Castner cell installations that are now operating, or have at one time operated, in countries other than the United Kingdom. However, a brief account of the development and operation of a Castner cell by the Niagara Electrochemical Company at Niagara Falls, N.J. has been given.[2] The cell appears to have been very similar to the Wallsend cell, operating at 7000 amp. and 4·3 V. This plant was shut down in 1925. A modified Castner cell has operated in Norway.[2a]

Little information is available regarding the Castner cell plant operated by the I.G. Farbenindustrie at Gersthofen, Germany. The electrolyte is described as caustic soda and the cell is said to operate at 330°C. at 4·5 V. at about 36% current efficiency, with an overall energy consumption of 21 kWh. per kg. of sodium, starting from sodium chloride.[7]

Mechanism of Electrolysis of Sodium Hydroxide.

The mechanism of the electrolysis of fused sodium hydroxide is discussed at length in the original Treatise (Mellor,II,6), and may be briefly summarized by saying that half the current is used to electrolyze water and that under normal running conditions the maximum possible efficiency of sodium production is 50%. Attempts made to exceed this efficiency by removing water from the anode compartment by means of a current of dry air,[8] or by structural changes to the anode and diaphragm[9] seem to have been unsuccessful in practice.[1] According to a recent patent, the loss of metal which takes place owing to reaction with water and oxygen at the cathode may be minimized by continually passing a portion of the fused electrolyte into a separate zone where it is heated to a temperature of 410°C., above that of the electrolysis zone (300-310°C.) in a countercurrent of dry air, thus vaporizing dissolved water from the electrolyte.[9a] It has been stated that the complete removal of the water from the electrolyte does not improve the yield of sodium, since the water is necessary to prevent pyrosol formation at the cathode, and laboratory experiments have shown that, when diffusion of the anodic water towards the cathode is completely suppressed by the addition of sodium to the anolyte or by interposing a zirconia diaphragm between the electrodes, current efficiencies approaching 100% are not obtained; on the contrary, the catholyte assumes a dark brown appearance and formation of hydrogen and sodium comes to a complete stop, the current efficiency falling to zero.[10] Wallace describes a similar phenomenon occasionally encountered in the operation of the Castner cell on the technical scale.[1] In this connexion it should be noted that the essential claim in Castner's original patent is that the temperature of electrolysis should be kept as near as possible to the melting point of the electrolyte, and in any case must not exceed it by 20°C.[1] If the removal of sodium from the cell is neglected and large amounts of metal are allowed to accumulate in the cell and the electrolyte is allowed to become too hot, a stage is reached when so much sodium has dissolved in the sodium hydroxide that the electrolyte starts to function as a metallic conductor and the current passes without producing any electrolysis. It is interesting to note that such a cell, which is described as being 'dead', can be revivified by the drastic but effective procedure of adding water to the electrolyte in the outer pot. The water dissolves in the electrolyte and reacts with the metallic sodium in solution to give sodium hydroxide, and electrolysis restarts. There seems, however, to be some doubt as to what happens when sodium dissolves in molten sodium hydroxide. According to von Hevesy, sodium dissolves in sodium hydroxide to form a true solution and the solubility decreases with increasing temperature. The rapid fall in current efficiency which takes place at tempertures above about 330°C. when electrolyzing fused sodium hydroxide is therefore not a result of the increased solubility of sodium in the electrolyte but is caused by the increased rate of diffusion of the metal in the electrolyte at higher temperatures (Mellor,II,448). Hevesy states that the metallic sodium can be deposited from its solution in sodium hydroxide by increasing the temperature[11] and a recent patent proposes to recover sodium from solution in sodium hydroxide in this way.[12] Other workers[13-13b] state that a reaction may take place between the sodium hydroxide and the sodium to form sodium monoxide and hydrogen if the temperature is sufficiently high, according to the equation: $NaOH + Na \rightarrow Na_2O + \frac{1}{2}H_2$. This reaction begins at 450°C. and proceeds vigorously at 550°C., but at the operating temperature of the Castner cell is likely to be extremely slow. Later workers,[14,15] studying the reaction of sodium with molten sodium hydroxide at temperatures corresponding approximately to Castner cell operating temperatures, find by *X*-ray studies that the sodium reacts with the hydroxide to form sodium monoxide and sodium hydride according to the equation:-

$$2Na + NaOH \rightarrow Na_2O + NaH.$$

Under these conditions the monoxide and the hydride remain in solution in the melt, and very little hydrogen is evolved.[16,17] A recent patent proposes the addition of sodium bromide or iodide, or a mixture of these two salts, to fused sodium hydroxide electrolyte, in the range of from 15 to 42 mol.-% in order to decrease the solubility of water in the electrolyte and so increase the current efficiency of electrolysis.[18] According to another patent, the secondary reaction that takes place on the electrolysis of fused sodium hydroxide, whereby the liberated hydroxyl ions combine to form water and oxygen, causing a marked decrease in current efficiency of sodium production, can be suppressed by carrying out the electrolysis in the presence of an auxiliary sodium salt, such a salt being able through a secondary chemical reaction to combine with the hydroxyl ion to reform the compound undergoing electrolysis with simultaneous production of gaseous products, such as ammonia, inert towards the molten electrolyte.[19,20] A suitable auxiliary salt is sodamide. Thus when fused sodium hydroxide is electrolyzed in the presence of fused sodamide the following reactions occur:-

1. $NaOH + (+)(-) \rightarrow Na^+ + OH^-$
2. $2OH \rightarrow H_2O + \frac{1}{2}O_2$
3. $H_2O + NaNH_2 \rightarrow NaOH + NH_3$.

The use of sodamide in the electrolysis of sodium hydroxide is advantageous in that the melting point of the bath is lowered, and the secondary reaction between sodium and water, which results in hydrogen formation, is suppressed. Moreover when sodamide is present the volume of gas evolution at the cathode is twice that obtained in the electrolysis of sodium hydroxide alone, and this favours the elimination as water vapour of part of the water produced by the electrolysis, so reducing the quantity of sodamide required for the fixation of water. It is claimed that the suppression of water formation at the anode more than doubles the current efficiency of sodium production.

It is stated that the efficiency of production of sodium by the electrolysis of sodium hydroxide tends to fall off as electrolysis proceeds owing to polarization. It has been proposed to overcome this effect by washing the cathode in water from time to time[21] or by periodic changes of polarity, the cathode becoming the anode for about 2 min. after the cell has been running for 8 to 12 hr.[21] It has also been proposed that when the electrolysis is carried out using a copper or copper alloy cathode and a slightly oxidized anode such as iron or nickel alloy, the cathode should be treated at intervals during the process to form a thin film of oxide and it is suggested that this may be done by reversing the current for a period of 2 to 10 seconds.[22,23] The effect of polarization in a Castner type cell has been studied on the semi-industrial scale by Pinck and Ledig, who found that the yield of sodium was increased by periodic inversions of the current for short periods.[21]

Influence of Impurities on the Electrolysis of Fused Sodium Hydroxide.

Wallace has discussed the effect of impurities in the electrolyte on the electrolysis of sodium hydroxide in the Castner cell.[1]

The purity of the sodium hydroxide used in the process is most important, and for satisfactory operation it is essential to use anhydrous sodium hydroxide made by a mercury brine cell process. Diaphragm cell sodium hydroxide is not recommended. For purposes of comparison typical analyses of diaphragm and mercury cell sodium hydroxide liquors are given below. It will be seen that the difference between the two materials is small, but nevertheless it appears to be sufficient to have a profound effect on cell operation.

The electrolysis of fused sodium hydroxide is especially sensitive to the presence of traces of sulphate, calcium or silica. According to Wallace,[1] when silica is present in the electrolyte, silicon is deposited at the cathode as the electrolysis proceeds, and this interferes with the operation of the cell. It is, however, uncertain how much sulphate can be tolerated, and cells have operated well with as much as 0·4% of sulphate in the bath. Similarly it is not known how much calcium can be tolerated in the electrolyte: cells have run well with as much as 0·046% of calcium carbonate in the electrolyte, but the addition of small quantities of calcium chloride rapidly reduces the yield of sodium and the electrolysis has been rendered completely unworkable by the use of sodium hydroxide to which 1 lb. of calcium oxide per ton of hydroxide was added during manufacture.[1] On the other hand the presence of sodium chloride and sodium carbonate in the electrolyte is beneficial and it is customary to work with a bath containing these materials.

TABLE III.- TYPICAL ANALYSES OF SODIUM HYDROXIDE[24,25]

Constituent	Concentration in Weight %		
	Diaphragm Cell Unpurified	Diaphragm Cell Purified	Mercury Cell
NaOH	50·00	50·2	50·00
Na_2CO_3	0·1–0·3	0·3	0·1–0·2
Na_2SO_4	0·013–0·02	0·02	0·0004–0·002
NaCl	1·0	0·16	0·002–0·01
$NaClO_3$	0·05–0·10	0·0004	-
CaO	0·0017	0·002	0·001–0·002
MgO	0·001–0·002	0·002	0·0001
Al_2O_3	0·0013–0·0030	0·003	0·001–0·0012
SiO_2	0·018–0·025	0·018	0·003–0·01
NH_3	-	0·0003	-
Fe	0·0005	0·0005	0·0001–0·0008
Ni	0·00003	0·00002	-
Cu	0·00003	0·00004	0·0002
Mn	0·00001–0·00006	0·00006	-
Hg	-	-	$< 10^{-6}$

ELECTROLYSIS OF FUSED SODIUM CHLORIDE

When Mellor wrote the original Treatise, the supremacy of the Castner cell as a means of manufacturing sodium was unchallenged, and although many attempts had been made to obtain the metal by electrolysis of fused sodium chloride, the efforts of the inventors had met with no permanent success. Since then, however, the position has been completely altered by the development of the Downs cell, and in these changed circumstances it may therefore be appropriate to give a brief account of the various steps that have led to the successful manufacture of sodium by electrolysis of fused sodium chloride. For more detailed information reference should be made to the numerous published accounts of the development of fused salt cell design and operation.[1-3,26-29]

The manufacture of metallic sodium by electrolysis of sodium hydroxide in the Castner cell suffers from at least two serious drawbacks. The maximum theoretical current efficiency which can be obtained from the cell, as operated under practical running conditions, is 50%, and the raw material used in the electrolysis is anhydrous sodium hydroxide, which for successful operation must have been made by the mercury brine cell route and is comparatively expensive.[1]

The principal and indeed almost the sole source of sodium in nature is common salt, and as a raw material this has a number of advantages over sodium hydroxide. Salt is considerably cheaper than the hydroxide, and is also more readily obtained in a pure condition. Moreover the electrolysis of sodium chloride yields not only sodium but also chlorine as a valuable by-product, and it is also possible to operate at higher current efficiencies than are attainable using sodium hydroxide.

There are, however, a number of very serious disadvantages attending the use of fused sodium chloride. Pure sodium chloride melts at about 804°C., and a considerably higher cell temperature must therefore be maintained during the electrolysis than is required in the Castner cell which operates about 310–320°C. Sodium boils at 880°C. and has a very substantial vapour pressure at 850°C., which is likely to be the approximate working temperature of a cell operating with an electrolyte of pure fused sodium chloride. Even at 600°C., which is about the operating temperature of some cells using low melting-point electrolyte baths, sodium burns very readily in air, and this complicates the design of the cell considerably. These high operating temperatures also create serious corrosion problems, and trouble is experienced from anode effect[30] and metal fog formation *i.e.* solution or dispersion of the sodium in the fused electrolyte.[26] Thus it is understandable that for many years processes intended for the manufacture of sodium by the direct electrolysis of fused sodium chloride proved to be unworkable when tried out on the industrial scale.

Attempts were made to overcome these difficulties in two different ways:-

1. The use of a molten metal cathode in which the liberated sodium dissolves to form an alloy, from which sodium may be recovered by subsequent treatment.
2. The addition of other salts to the fused bath in order to get a low-melting electrolyte.

As might be expected, the above methods of working, while eliminating some of the disadvantages attached to the direct electrolysis of pure fused sodium chloride, introduce in their turn other difficulties which in some cases have been found to outweigh the advantage gained.

From about 1890 to about 1909 most work seems to have been directed towards the development of cells employing a molten metal cathode. The first successful cell of this type was the Acker cell[31] where fused sodium chloride was electrolyzed in the presence of a molten lead cathode to give a sodium–lead alloy which was then denuded by steam in a separate compartment to give anhydrous sodium hydroxide. The cell suffers from the drawback that it does not in fact manufacture metallic sodium except in the form of a sodium–lead alloy, from which the sodium is recovered not as the metal but as the hydroxide. This type of cell may be considered the high temperature analogue of the Castner cell for the electrolysis of brine, molten lead replacing the mercury, and the recovery of anhydrous sodium hydroxide by treatment of the sodium-lead alloy with steam corresponding to the denuding of the amalgam with water.

An Acker cell plant with a maximum output of about 6 tons of sodium per day ran for several years at Niagara in the United States, but was eventually completely destroyed by fire in the year 1907 and was never restarted.[26]

The Ashcroft cell,[32] which was at one time subjected to full-scale tests in Norway, consisted of two compartments. In the decomposing compartment fused sodium chloride was electrolyzed and the liberated sodium dissolved in a molten lead cathode. This alloy was then circulated to a producing compartment where it served as anode in a bath of molten sodium hydroxide. On electrolysis the sodium passed into the electrolyte and was re-deposited on a nickel cathode submerged in the melt. A hood immediately above this cathode collected the globules of sodium which rose in the melt from the cathode, and this sodium then overflowed through a pipe into a receiver. The cell therefore produced metallic sodium and not merely a sodium-lead alloy. Ashcroft used a crude salt, and this gave rise to deposition of impurities on the molten cathode which led to increased voltage troubles. The process did not become established commercially.

The molten metal cathode routes to sodium failed to obtain lasting success on the commercial scale and may be considered, in the words of Hardie,[26] to represent a false start to the solution of the problem of the electrolysis of fused sodium chloride.

However, an interesting recent industrial development, whereby a fused sodium chloride-potassium chloride mixture is electrolyzed in the presence of a molten lead cathode in order to produce a sodium-lead alloy, suggests that in some circumstances this route may offer advantages over the now well established electrolysis of sodium chloride-calcium chloride electrolytes.[7]

Following the failure of the molten metal cathode routes to establish themselves, attention was once again directed toward the direct electrolysis of fused sodium chloride, either in the pure state or in electrolyte mixtures of lower melting point.

In 1924 Danneel described work carried out prior to the 1914-1918 war on the large scale production of sodium by the electrolysis of sodium chloride.[27,28,33] The electrolysis was carried out in a bath consisting of 72% of sodium chloride, 10% of potassium fluoride and 18% of sodium fluoride, melting at 610°C. Sodium so made always contains a small amount of potassium, but very little fluorine is produced at the anode. It is said that the formation of fluorine is undesirable as it reacts with the graphite of the anode to give carbon tetrafluoride. Other bath compositions were tried. A mixture of 70% of sodium chloride and 30% of potassium fluoride melts at 550°C. but on electrolysis gives a product containing about 2% of potassium: there is, however, no fluorine in the chlorine simultaneously liberated. An electrolyte containing 6·5% of potassium and 11·7% of fluorine gives a metal resembling pure sodium but containing 0·5-0·6% of potassium, and the chlorine liberated contains appreciable amounts of fluorine.

More recently other fluoride-containing electrolyte baths have been proposed for the electrolysis of sodium chloride.[34] Thus sodium has been made by the electrolysis of a mixture of 62·5% of sodium chloride, 12·5% of potassium chloride and 25% of sodium fluoride. The electrolysis is carried out in a talcochlorite-lined cell at 620-650°C., and is said to proceed normally even at anode current densities as high as 0·3 to 0·5 amp. per sq. cm.

About 1909 the so called 'Ciba' cell was developed in Switzerland by the Gesellschaft für chemische Industrie in Basel.[35,36] The electrolyte was fused sodium chloride, or mixtures thereof with other salts, and the sodium and chlorine produced by the electrolysis were separated by means of a diaphragm or diaphragms. The cell carried an arrangement of heating resistances and additional electrodes for melting the electrolyte by means of alternating current. The cell operates at about 6000 amp. and 10–11 V. with an energy consumption of about 2500 kWh. per 100 kg. of sodium.[36] The Ciba cell is shown diagrammatically in Fig. 3. It may be regarded as a modified Castner

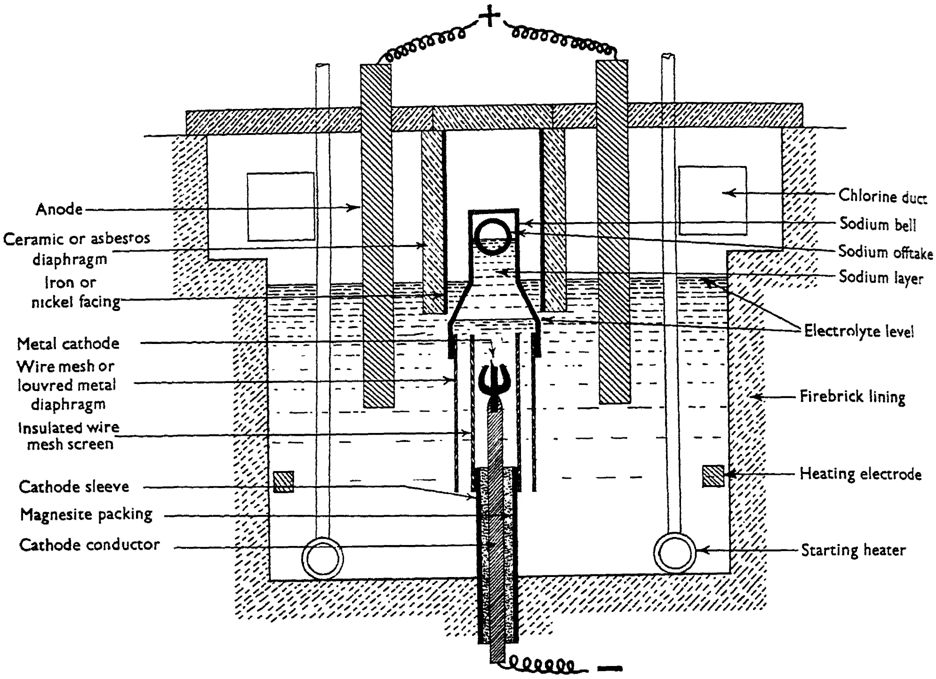
+
Anode
Ceramic or asbestos diaphragm
Iron or nickel facing
Metal cathode
Wire mesh or louvred metal diaphragm
Insulated wire mesh screen
Cathode sleeve
Magnesite packing
Cathode conductor
Chlorine duct
Sodium bell
Sodium offtake
Sodium layer
Electrolyte level
Firebrick lining
Heating electrode
Starting heater
—

FIG. 3. CIBA SODIUM CELL

cell adapted to the electrolysis of fused sodium chloride. In 1926 the output of Ciba cell sodium was about 500 tons per year, so that the cell must be considered to have attained a fair degree of technical success.[35] No recent production figures are available.

The McNitt cell, shown in Fig. 4, was patented in 1917: it appears to represent a considerable advance and may be considered the forerunner of the Downs cell.[37] In this cell the collecting chamber is submerged in the electrolyte to such a depth that the liberated sodium, which is considerably less dense than the electrolyte, automatically rises up a pipe to a level at which it overflows into a receiving vessel. The cathode is located centrally inside the anodes, and the cell is fitted with a diaphragm which serves to separate the sodium deposited at the cathode from the chlorine liberated at the anode. Later patents by McNitt propose a number of modifications in cell design which would appear to be equally applicable to other fused halide cells such as the Downs cell.[38-43a]

The Downs cell, patented in 1924,[44] succeeded in solving the problem of making sodium by the electrolysis of fused sodium chloride, and has been extensively adopted on the commercial scale, not only in the United States where it originated, but also in a number of other countries including England and Germany. The basic Downs cell is shown diagrammatically in Fig. 5. A number of modifications to the cell have been described in patents.[41-43,45-47]

The Downs cell, like that of McNitt, makes use of a hydrostatic head of

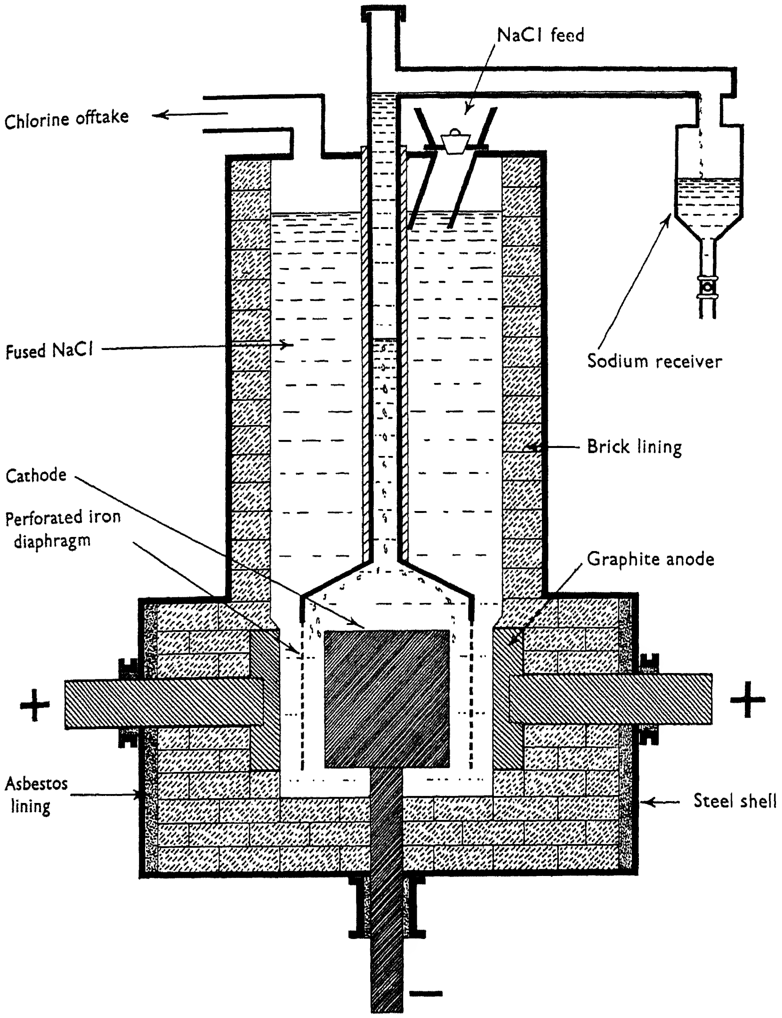
NaCl feed
Chlorine offtake
Fused NaCl
Sodium receiver
Brick lining
Cathode
Perforated iron diaphragm
Graphite anode
+
+
Asbestos lining
Steel shell
−

FIG. 4. MCNITT SODIUM CELL

electrolyte to ensure that the sodium produced may be removed from the cell continuously and automatically, but it is distinguished from the Castner cell, the McNitt cell and many others devised for the electrolysis of sodium chloride by the novel feature that the anode is located inside the cathode. A considerable amount of information has been published regarding the modified type of Downs cell operated at Knapsack near Cologne in Germany by the Deutsche Gold- und Silberscheideanstalt vormals Roessler, commonly referred to as 'Degussa', and many details of design, construction and operation are given.[36,48,49] American cells have also been described, but in considerably less detail.[29] The design of the American cells differs somewhat from that of the German cell. The Knapsack cell is illustrated in Fig. 6 and is briefly described below. For further details the reader should consult the original publications on the subject. A Downs cell installation in England has also been described.[49a,b]

The body of the cell is a steel shell lined with refractory brick. A com-

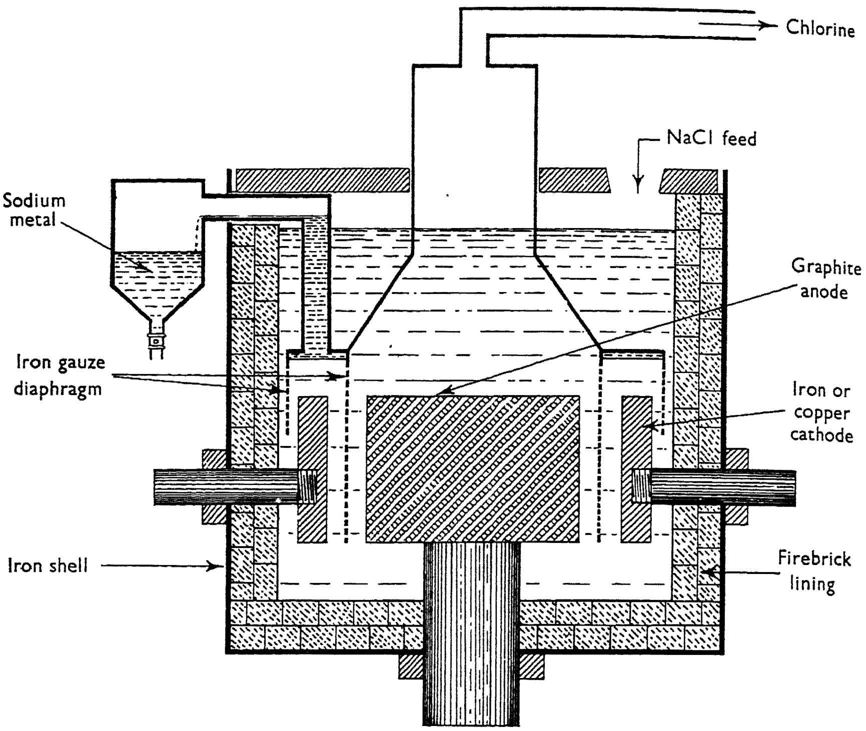

FIG. 5. DOWNS SODIUM CELL
AFTER U.S. PATENT NO. 1,501,756

posite cylindrical graphite anode assembly consisting of a number of accurately machined pieces of graphite, bolted together to give a square cross section at the bottom, projects upward through the cell bottom and is located centrally in the cell where it is surrounded by the cathode. In the case of the 24,000 amp. cell this assembly is made up of 8 graphite pieces, whereas in the 32,000 amp. cell only 4 pieces are used. The cathode is a cylindrical ring of cast steel, supported by two arms extending through the sides of the cell body to the electrical connexions. A conical brick-lined bell or dome, submerged in the electrolyte and situated directly above the anode, serves to collect the chlorine. A diaphragm suspended from the dome into the electrolyte prevents the sodium coming in contact with the chlorine. The diaphragm is made of 16 mesh steel gauze and is fitted with stiffening bands to help it to retain its shape at the temperature of the cell. Somewhat surprisingly this steel gauze does not appear to be appreciably attacked by the hot dry chlorine produced during the electrolysis. The dome also carries an inverted trough, located over the cathode, which collects the sodium. This sodium collector is submerged in the electrolyte so that the sodium produced by the electrolysis rises upward, by virtue of the difference in density between molten sodium and the electrolyte, through a riser pipe, and overflows into an external receiver. This riser pipe is cooled by radiation and this reduces the temperature of the sodium flowing through it.

The electrolyte bath is a mixture of about 42–41% of sodium chloride and 58–59% of calcium chloride the low melting-point of which enables the cell to operate at about 590 ± 5°C.[48] A number of patents describe devices for ensuring that an adequate circulation of electrolyte in the electrode gap is

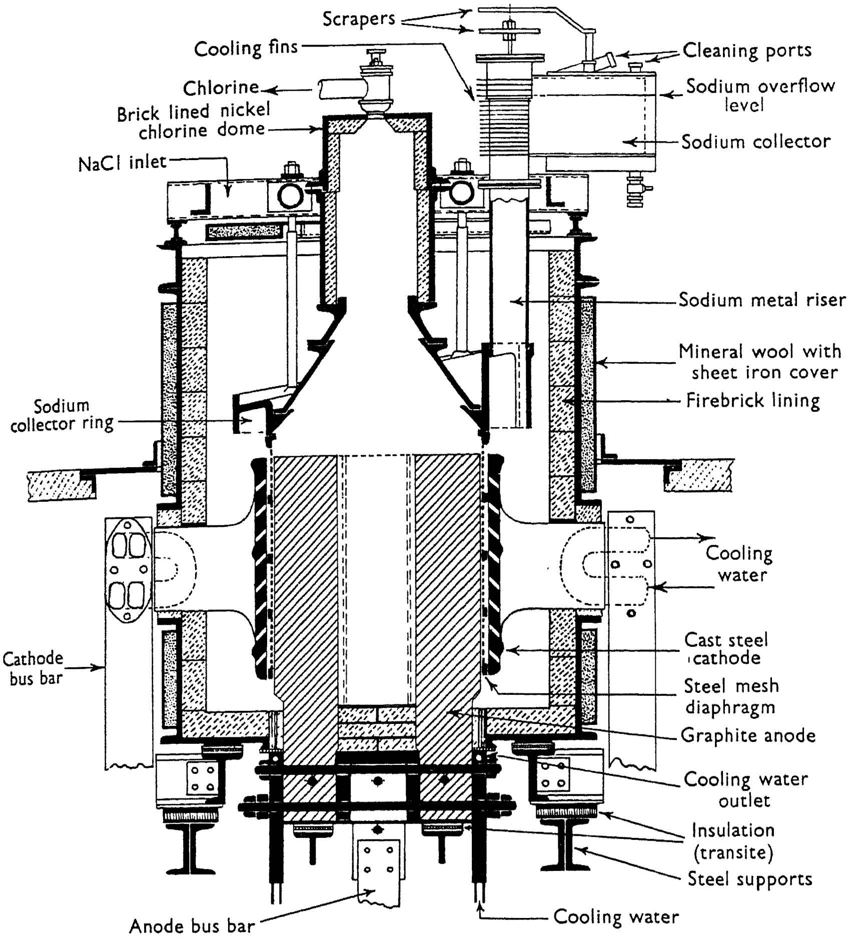
Scrapers
Cooling fins
Chlorine
Brick lined nickel chlorine dome
NaCl inlet
Cleaning ports
Sodium overflow level
Sodium collector
Sodium metal riser
Mineral wool with sheet iron cover
Firebrick lining
Sodium collector ring
Cooling water
Cathode bus bar
Cast steel cathode
Steel mesh diaphragm
Graphite anode
Cooling water outlet
Insulation (transite)
Steel supports
Anode bus bar
Cooling water

FIG. 6. KNAPSACK 24,000 AMP. SODIUM CELL

maintained.[38,40,47-47b] Dry sodium chloride is fed continuously to the cell during electrolysis.[48] The sodium initially produced by the cell contains a few per cent. of dissolved calcium metal which, owing to the limited solubility of calcium in sodium at lower temperatures, is deposited as the sodium ascends the riser or cooling pipe. Owing to its comparatively high density as compared with liquid sodium, the calcium deposited sinks back into the electrolyte where it reacts to form the equilibrium alloy.[48,51-53] The purification of the sodium is described later (see page 344).

The cell is insulated from the ground to prevent current leakage, and the mobile sodium-collecting receiver has rubber tyres for insulation. The chlorine produced by the cell is removed under slight suction.

The Knapsack plant consisted of 65 Downs cells operated in two banks, one of about 40 and the other of 25 cells. In 1946 the standard cell at Knapsack was of 24,000 amp. capacity but experimental cells of 27,000 amp. and 32,000 amp. were also in existence. Operating details of the cell are summarized in Table IV (see page 345). It has been stated that in 1954 Downs cells generally operate at 28,000–35,000 amp., the trend in recent years being towards an even higher capacity.[26]

The amount of calcium carried out of the cell into the sodium receiver has been much reduced by providing external cooling fins on the cell riser pipe, so that the sodium-calcium alloy, produced in the cell at temperatures around 600°C., is cooled to about 100-200°C.[52] As the alloy ascends the pipe the temperature falls, till a stage is reached where the concentration of calcium exceeds its solubility in sodium, when it is precipitated and falls back into the cell. An automatic device for removal of deposits from the sodium riser pipe has been patented.[52a,b]

The separation of electrolyte and sedimentary impurities from the sodium before it leaves the cell has been the subject of a number of patents.[55-60]

According to one source, the calcium content of the sodium leaving the cell is about 0·5-1·0%.[26] On the other hand, a patent gives the following figures for the calcium content of sodium leaving a cell.[61]

Temperature of liquid sodium leaving the cell °C.	% Calcium in the sodium leaving the cell
210	0·21
170	0·20
160	0·20
135	0·15

This sodium is then further purified by cooling it to about 110°C., at which temperature the solubility of calcium in sodium is very low, and filtering it (see also page 352). After filtration the sodium contains about 0·04% of calcium.[48,54,62,63] According to a patent, further purification from calcium may be effected by subjecting the molten sodium to the action of an oxidizing agent, such as air, at a temperature not lower than 350°C., to convert the calcium to calcium oxide[64] which is then separated from the sodium by filtration after cooling to a temperature just above the melting point[64] (see page 358).

In another patent it is proposed that the sodium-calcium alloy from the cells should be freed from calcium by passing it over solid sodium chloride at 500-700°C. when the calcium reacts with the sodium chloride to form calcium chloride and metallic sodium.[65,66]

The residues accumulating on the filter, generally known as Downs cell sludge, are removed from time to time and treated in a hydraulic press which serves to remove most of the sodium. The final residue from the press is then returned to an old cell approaching the end of its useful life where sodium is recovered according to the equation:[48,68-74] $Ca + 2NaCl \rightarrow CaCl_2 + 2Na$. Other methods of treating cell sludge are discussed later (see page 352).

The Knapsack cells are operated in the following manner.[48] Before a new cell is started up, the brickwork is thoroughly dried out for a week by a low charcoal fire burned in the space between the anode and the brickwork. The cell is then started up without the sodium collector ring, diaphragm etc. being in place. Four graphite wedges are placed 90° apart between the anode and the cathode and the cell is filled with broken lumps of solidified electrolyte. Full current is then passed through the cell, and the heat developed is sufficient to melt the electrolyte. During this operation a hood is placed over the cell and connected to the vent suction line in order to remove the unpleasant fumes formed. When the cell is full of molten electrolyte at about 600°C. the graphite wedges are withdrawn, the hood is removed, and the chlorine and sodium collecting assembly, together with the diaphragm, installed. The chlorine produced directly after a cell starts up tends to be of low concentration for several days and is consequently removed via the dilute

TABLE IV. - OPERATING DATA FOR KNAPSACK DOWNS CELL

	24,000 amp. Cell	32,000 amp. Cell
Production		
Sodium metal per day	385 kg.	515 kg.
Chlorine per day	590 kg.	790 kg.
Electrolyte		
Calcium chloride	58–59%	58–59%
Sodium chloride	42–41%	42–41%
Current efficiency	78%	-
Voltage, starting	5·7 V.	-
Voltage, final	6·0 V.	-
Sodium per kWh. without copper loss	88·2 g.	-
Sodium per kWh. including copper loss	87·2 g.	-
Calcium chloride usage per 100 kg. sodium	4·0 kg.	-
Cells		
Material of construction	Steel, acid-proof brick lined	Steel, acid-proof brick lined
Dimensions of steel shell (inside)	1620 mm. diam. × 2010 mm. depth	1620 mm. diam. × 2307 mm. depth
Brick lining, Durex II (acid proof brick): thickness	105 mm.	105 mm.
Insulation	40 mm.	40 mm.
Overall cell height (bus bars to sodium collector)	3798 mm.	4345 mm.
Cell temperature	585–595°C.	-
Sodium collector temperature	200–250°C.	-
Anodes		
Material of construction	Graphite	Graphite
Length	1464 mm.	2029 mm.
Cross section, each piece	254 × 284 mm.	410 × 410 mm.
Approx. weight	1200 kg.	2130 kg.
Number	8	4
Diameter inside cell	840 mm.	690 mm.
Current contact height	280 mm.	406 mm.
Sealing surface through steel height	180 mm.	322 mm.
Graphite consumption per kg. of sodium	1·6–1·9 kg.	-
Cathodes		
Material of construction	Cast steel	Cast steel
Outside diameter	995 mm.	1066 mm.
Inside diameter	914 mm.	966 mm.
Height	864 mm.	1150 mm.
Cathode current density	9700 amp./m.^{2}	9700 amp./m.^{2}
Diaphragms		
Material of construction	16 mesh iron and steel	16 mesh iron and steel
Outside diameter	876 mm.	926 mm.
Height	939 mm.	1208 mm.
Life, in days	20–30	-

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gas main. When the cell is operating normally the gas produced contains about 92–96% of chlorine, the rest being air and small quantities of carbon oxides from oxidation of the anode.

A new cell starts up with a voltage of 5·7 V., but as the anodes wear this gradually increases to about 6 V. When the cell is first started up, all the thermal insulation is in place, and the temperature of the electrolyte is about 585°C. This cell temperature is measured twice a week during the life of the cell, and, as the voltage increases owing to anode wear, the temperature rises owing to the increased resistance of the electrolyte and the cell insulation, which is in two halves, one above and one below the operating floor, is removed, the bottom section being taken away first. Finally, in spite of the removal of the insulation, it is found that the electrolyte temperature rises to 595°C. at 6 V.; the cell is then considered to have reached the end of its useful life and is accordingly shut down.

The cell life is given as 300–350 days, and it takes two or three days to dismantle an old cell and instal a new one. During cell operation it is found that the voltage may rise suddenly to 8·5–9 V., and this is rectified by changing the diaphragm. Failure of the diaphragm has not been satisfactorily attributed to a single cause and it is suggested that it results from a number of chemical and thermal effects. According to a patent, the need for a diaphragm in the production of sodium by the electrolysis of fused chloride may be eliminated by the use of a porous carbon electrode with a centre cavity and gas conduit for removal of the chlorine during electrolysis.[48a]

A diaphragm lasts about 20 to 30 days, and the cell is out of production for about 4 hours while the change is being made. During this period the assembly which carries the diaphragm is removed from the cell and the electrolyte is filtered through a conical 16 mesh steel gauze filter. This filter is suspended above the cell and the electrolyte pumped from the bottom of the cell into the filter by means of an airlift using dry air. This airlift arrangement is also used to empty a cell which has reached the end of its useful life, when the electrolyte is discharged into iron vessels and after solidification is used as charging material for starting up a new cell. Operational conditions vary. Thus, in the United States the cell is described as operating at about 7 V. with a current efficiency of about 80–85%.[29] This corresponds to an energy consumption of 5 kWh. of a.c. power per pound of sodium, after allowing for a 6–8% loss in converting from a.c. to d.c. power.[29]

Determination of the back e.m.f. and calculations based on thermodynamical data indicate that the decomposition voltage of the cell is about 3·45 V. and the difference between this figure and the actual cell voltage is therefore required to overcome the resistance of the electrolyte, and electrode connexions etc.[26]

Hardie gives the following comparison of the energy efficiency of the Castner and the Downs cell.[26] Assuming a current efficiency of 80% and a working voltage of 7, the energy efficiency of the Downs cell is approximately 39%. If the figure 6 is taken as the voltage for the Knapsack cell, the energy efficiency becomes about 46%. With the Castner cell the highest efficiency obtained is about 24%, and as the sodium hydroxide used in the cell is produced from salt electrolyzed in a brine cell at an efficiency of about 60%, the overall efficiency is at best only slightly over 14%. The energy efficiency of the Downs process is therefore about three times that of the two stage Castner process from salt to sodium. This being so, it is scarcely surprising that the Castner process, after many years of unchallenged supremacy in production of electrolytic sodium, is now almost completely superseded by the Downs cell, and may be expected to become obsolete before long.

Purity of Downs Cell Sodium.

The sodium produced by the Downs cell attains a degree of purity seldom found in a commercial material. The sodium content of the metal is 99·95%,[75] and the following are present as impurities:-[75]

	%
Silicon	0·007
Iron	0·002
Calcium	0·012
Boron	0·05
Chlorine	0·0067
Nickel	0·0004
Aluminium	0·0001
Phosphorus	0·005
Sulphur	0·009
Heavy metals	0·028
Hydrogen[76]	0·006

Small amounts of sodium oxide and hydroxide are also present. Degussa also produce a special quality of sodium which contains less than 0·001% of calcium. This is made from the ordinary Downs cell sodium by a purification process.[36]

Downs Cell Chlorine.

The Downs cell produces chlorine in addition to sodium. For a discussion of the handling and purification of chlorine produced by electrolysis the reader is referred to Volume II, Supplement 1.

The Downs Cell Electrolyte.

The composition of the electrolyte bath used in the Downs cells operated in the United States differs from that adopted in Germany. Thus, in the United States the cells work at approximately 600° C. with an electrolyte consisting of a eutectic of 66·8% of calcium chloride and 33·2% of sodium chloride[29] whereas German practice favours an electrolyte containing 58–59% of calcium chloride and 41–42% of sodium chloride with an operating temperature of 585–595° C.[48]

The sodium chloride used in the cell must be anhydrous and free from sulphate.[48] In Germany this feed salt is purified by dissolving rock salt in water and treating the solution with barium carbonate and caustic soda. The treated brine is then filtered and evaporated in triple effect evaporators, after which the salt is removed as a slurry, centrifuged and dried at 300–400°C. before being stored. About 105–110 kg. of crude salt and 0·091 kg. of barium carbonate are required to produce 100 kg. of refined salt. No figure is given for caustic soda consumption.[48]

A method has been patented for the purification of a halide such as sodium chloride, for use in an electrolytic cell, by heating it and fusing it in a compartment of the cell, separated from that in which electrolysis takes place, in order to remove moisture and impurities capable of being volatilized under these conditions.[77]

A make-up of calcium chloride equivalent to about 4 kg. per 100 kg. of sodium produced must be added to the electrolyte to replace the calcium removed in solution in the sodium.[48]

The fundamental reaction taking place on electrolysis of fused sodium chloride is very simple and may be represented thus:-

$$\underset{\text{(liquid)}}{2\mathrm{NaCl}} \rightarrow \underset{\text{(liquid)}}{2\mathrm{Na}} + \underset{\text{(gas)}}{\mathrm{Cl_2}}$$

In the Downs cell, however, matters are more complicated owing to the presence of calcium chloride in the electrolyte, and the equilibrium $CaCl_2$ + 2Na ⇌ 2NaCl + Ca must also be considered. The first quantitative study of this equilibrium appears to have been made by Jellinek and Czerwinski.[78] These workers did not use pure calcium and sodium, however, but alloys with a large excess of lead, and it is therefore needless to consider these results further. Lorenz and Winzer examined the equilibrium at temperatures varying between 600°C. and 800°C., and give the following figures for the equilibrium at 500° and 600°C. (Table V).[79,83]

TABLE V.- EQUILIBRIA IN THE REACTION:
$CaCl_2 + 2Na \rightleftharpoons 2NaCl + Ca$

Molecular % Sodium chloride	Molecular % Calcium chloride	Atomic % Sodium	Atomic % Calcium
Equilibrium at 500°C.			
48·1	51·9	99·49	0·51
48·4	51·6	99·12	0·88
49·4	50·6	99·06	0·94
48·0	52·0	99·13	0·87
Equilibrium at 600°C.			
47·3	52·7	98·80	1·20
46·5	53·5	99·09	0·91
55·8	44·2	99·51	0·49
56·8	43·2	99·22	0·78

According to these results the equilibrium concentration of calcium in sodium at Downs cell working temperatures is not likely to exceed about 1 mole per cent. Lorenz and Winzer also claim, however, that over a considerable range variation in the composition of the salt phase is not accompanied by any change in the total composition of the metal phase. The equilibrium has more recently been investigated in much greater detail by Rinck[80] who points out that Lorenz and Winzer's results do not obey the Phase Rule. Rinck considers that the conditions under which these authors carried out their experiments were likely to produce inaccurate results. He points out that the starting materials were sodium and calcium chloride, and that it is difficult to obtain calcium chloride in the pure state. Moreover, Lorenz and Winzer worked in Jena glass which, while it has an appreciable mechanical resistance at 800°C., is nevertheless heavily attacked by the equilibrium mixture, and because of the absorption of air by the calcium the glass tubes were flattened by external pressure which rendered good separation of the phases impossible. Rinck on the other hand worked with pure calcium and pure sodium chloride as starting materials, and in steel tubes which readily withstood the highest temperatures and were not attacked by the equilibrium mixture. Unfortunately Rinck studied the equilibrium only at 712°C. and higher temperatures, and no results are available for Downs cell working temperatures, but he gives the following values for the solubility of calcium in sodium:-

Temp. °C.	Atomic % calcium
1100	16·5
975	10·85
850	7·26
712	4·0

By extrapolation from these data a value of about 4·0 weight-% may be inferred for the solubility of calcium in sodium at 600°C., which may be regarded as approximately the cell working temperature. According to another source the solubility of calcium in sodium at 600°C. is about 5·5 weight-%.[29]

Thus, the metal phase in the Downs cell is not pure sodium but an alloy of sodium and calcium, the composition of which will depend on the respective concentrations of sodium chloride and calcium chloride in the electrolyte, and on the cell temperature.

The amount of calcium in the Downs cell sodium is not known, but calculations based on the calcium–sodium equilibrium diagram and thermodynamical data indicate a concentration of 3–4 weight-% at the eutectic composition,[26] 66·8% of calcium chloride, as used in America.[29] With the German electrolyte containing 58% of calcium chloride the calcium content of the sodium may differ from that in the American cells. In neither case, however, can the equilibrium concentration of calcium exceed the solubility of calcium in sodium, since otherwise deposition of calcium would occur in the cell.

The solubility of calcium in sodium has been given as 1·38 weight-% at 700°C.,[79] 6·76 weight-% at 700°C.[80] and more recently as 5·5 weight-% at 600°C., falling rapidly to about 4 weight-% at 400°C. and 0·01 weight-% at the melting point of sodium, 97·5°C.[29]

The so called fog formation resulting from the solubility in the electrolyte of the metal produced by the electrolysis is of great importance in practice, since it leads to current inefficiency, as sodium chloride is reformed from the sodium in solution by reaction with the liberated chlorine at the anode. Workers who have attempted to prepare sodium by fused salt electrolysis constantly comment on this source of loss, which is greatly increased as the temperature is raised, probably owing to the increased solubility of sodium or, in the case of the Downs cell, sodium–calcium alloy in the electrolyte.[26]

Some workers claim that the metal in such circumstances disperses itself in the molten salt in the form of a fog or pyrosol[79] whilst others state that the effect may be attributed either to true solution,[81] or to the formation of a subhalide at high temperatures:-[82]

$$CaCl_2 + Ca \rightleftharpoons 2CaCl.$$

Lorenz and Winzer found that the solubility of sodium in fused sodium chloride is 4·2 and 15·2 weight-% at 800°C. and 850°C. respectively, whilst at slightly higher temperatures the metal phase and the salt phase become completely miscible.[83]

Recent determinations on the equilibria between molten sodium and molten sodium chloride have given the following figures:-[84]

Temperature °C.	Salt phase Mole % Sodium
803	2·4
809	2·8
826	4·9
990	10·2

Evidently the equilibrium concentration of sodium increases very rapidly as the temperature rises.

In the case of the system calcium–calcium chloride, the components form a eutectic containing 1 mole % of calcium at 767°C.[81]

Solubilities of sodium in sodium chloride–calcium chloride melts are given in Table VI.[79,83]

TABLE VI.- SOLUBILITY OF SODIUM IN SODIUM CHLORIDE-CALCIUM CHLORIDE MELTS

Salt Phase Molecular %		Metal Phase Molecular %		Sodium + Calcium as wt. % Sodium
Sodium Chloride	Calcium Chloride	Sodium	Calcium	
	Solubility at 700°C.			
33·5	66·5	99·25	0·75	3·4
33·6	66·4	99·31	0·69	4·7
46·6	53·2	99·26	0·74	4·6
57·2	42·8	99·44	0·56	4·5
66·2	33·8	99·48	0·52	4·3
65·8	34·2	99·56	0·44	4·2
	Solubility at 600°C.			
47·3	52·7	98·80	1·20	3·3
46·5	53·5	99·09	0·91	2·7
55·8	44·2	99·51	0·49	2·7
	Solubility at 500°C.			
48·1	51·9	99·49	0·51	0·4
48·4	51·6	99·12	0·88	0·6
49·4	50·6	99·06	0·94	1·2
48·0	52·0	99·13	0·87	0·4

It has been said that perhaps the greatest difficulty confronting experimenters in the electrolysis of fused sodium chloride is the solution of sodium in fused halide mixtures at temperatures above 700° C.[26] The advantage of operating at a lower temperature is clearly illustrated by the results.

A device for the temperature control of fused electrolyte cells consists of a heat transfer unit employing a vaporizable liquid metal. A sealed tube containing sodium is partially submerged in the electrolyte. The sodium evaporates and condenses on the colder upper portion of the tube where heat is lost by radiation, and runs back into the lower portion of the tube, thus providing regenerative cooling.[26a]

Decomposition Voltage of Sodium Chloride and Calcium Chloride.

The following values for the decomposition voltage of sodium chloride have been obtained by measuring the current flow across fused sodium chloride between graphite electrodes with gradually increasing voltages:-[85,86]

Temperature	835° C.	870° C.	970° C.
Decomposition voltage	2·6	2·55	2·4

Cambi and Devoto[87] determined the decomposition voltage by measuring the electrometric force immediately after cessation of the electrolysis, and obtained results which differ appreciably from the above. They claim that their results are in agreement with the known physical data for chlorine and sodium, and attribute Neumann's low results to depolarization. They also found that the decomposition voltage varied according to the nature of the cathode, as will be seen from the following results:-

Temperature	800°C.	850°C.	900°C.	950°C.	1000°C.
Decomposition voltage, using a copper cathode	3·254	3·180	3·107	3·033	2·96

continued on following page.

Temperature	800° C.	850° C.	900° C.	950° C.	1000° C.
Decomposition voltage, using an iron cathode	3·200	3·129	3·058	2·987	-
Neumann, using a graphite cathode	2·65	2·58	2·51	2·43	2·36

By extrapolation from the results given, the decomposition voltage of sodium chloride at 600°C. is 2·93 V. (Neumann) or 3·48 V. (Cambi and Devoto). In the case of calcium chloride the following figures are given:-[67]

Temperature	780° C.	804° C.	830° C.
Decomposition voltage	3·314	3·228	3·18

By extrapolation, the decomposition voltage at 600° C. is 3·67 V.

Data have been recorded on the density, viscosity, specific conductivity and surface tension of sodium chloride-calcium chloride melts at temperatures varying from 500° to 1000° C. and from 0 to 100% of calcium chloride.[88-88d] and on the density of the binary electrolytic bath sodium chloride-calcium chloride for varying proportions of the salts over the temperature range 550-850° C.[89] The mechanism of the cathodic process in the electrolysis of a fused sodium chloride-calcium chloride melt, using an iron cathode, has been studied.[89a]

The effect of small amounts of potassium chloride on the conductivities of calcium chloride-sodium chloride mixtures has been studied.[88e,f]

Influence of Electrolyte Impurities on Electrolysis.

Little information has been published regarding the influence of impurities in the electrolyte on Downs cell operation. The presence of soluble oxygen-containing compounds appears to be detrimental to cell efficiency, however, as such impurities are decomposed at the anode during the electrolysis with the liberation of oxygen or other harmful substances which may attack or corrode the active surface of the anode with consequent increase in cell voltage. Alternatively the impurities may form soluble secondary substances which are in turn decomposed by the current, thus initiating a cycle which may reduce the current efficiency to a small fraction of that attainable when such impurities are absent.[90]

Danneel's observations on the influence of oxygen-containing compounds in low melting-point sodium chloride baths containing fluorides[27] are probably equally applicable to calcium chloride-sodium chloride melts. He remarks that it is desirable to avoid oxidation of the sodium produced during the electrolysis. When sodium oxide is formed it tends to dissolve in the electrolyte where it is electrolyzed:-

$$2Na_2O \rightarrow 4Na + O_2.$$

The oxygen is liberated at the anode where it combines with the graphite of the anode to give carbon monoxide, thus accelerating anode wear and reducing cell life. The carbon monoxide so produced also tends to react with chlorine to give phosgene.[27]

Dissolved sodium oxide in the electrolyte also attacks the silica of the cell lining to give a silicate which in turn is electrolyzed according to the equation:-[27]

$$2Na_2SiO_3 \rightarrow 4Na + 2SiO_2 + O_2.$$

The silica and oxygen are formed at the anode, where the oxygen reacts to give carbon monoxide and the silica is reduced to silicon, which ultimately appears as silicon tetrachloride in the chlorine evolved during electrolysis.[27]

According to a patent, when sodium is being produced by the electrolysis of fused salt baths containing substantial amounts of sodium chloride, the bath may be kept free from sodium oxide by adding small quantities of a metal, or a metal compound, which can react with the sodium produced or with its oxide to give a compound insoluble in the cell bath.[91,92] Thus, alumina may be used to keep the cell bath substantially free from oxide.[91] The addition of aluminium or calcium to the bath feed compartment has also been proposed;[90] in this case the oxygen compounds formed are only partially soluble in the molten electrolyte and can be sludged out of the cell. Impurities may also be removed by a secondary electrolysis of the cell bath.[90]

Downs Cell Sludge.

The use of a sodium chloride–calcium chloride bath in the Downs cell has the advantage of permitting electrolysis at a comparatively low temperature. There are, however, accompanying disadvantages attached to the use of such an electrolyte mixture, and one of the most serious arises because the equilibrium mixture of sodium and calcium produced in the cell contains several per cent. of calcium. Moreover, sodium chloride is slightly soluble in molten sodium at the operating temperature and the metal is therefore likely to contain small amounts of the salt phase in solution.[29,48,84] These impurities are largely eliminated by cooling the metal mixture to 100–120°C., before it leaves the cell[48] (see also page 343). The substantially pure sodium thus obtained is further purified by filtration to give sodium containing only about 0·04% of calcium, and the residue from this filtration is a mixture of sodium with considerable quantities of calcium metal, generally termed 'Downs cell sludge'.

The disposal of this sludge presents a considerable problem, and a number of patents have been filed describing procedures or devices for reducing the calcium content of the sodium leaving the Downs cell and so minimizing the amount of sludge produced on subsequent filtration.[51-53,56-61]

One claims that if the sodium is filtered in the molten state through a filter medium across which a pressure difference is maintained, satisfactory filtration can be achieved with a relatively coarse filter medium having openings which are larger than a substantial proportion of the alkaline earth metal particles present in the sodium.[62-63a]

Sodium may be recovered by introducing the sludge into a bath of molten salt having a density higher than that of sodium, containing calcium chloride together with over 30% of sodium chloride, at a temperature of 600–800°C.[67-69] Reaction takes place between sodium chloride and calcium to give sodium metal which, together with the sodium already present in the sludge, floats to the top of the bath and may be collected. If the operation is carried out efficiently the sodium should contain less than 0·1% of calcium.

The purification may also be conveniently accomplished by introducing the sludge into a fused mixture of sodium chloride and calcium chloride which is undergoing electrolysis in an electrolytic cell such as the Downs cell, and this appears to offer a simple means of disposal.[70-72]

An apparatus for the separate recovery of sodium and calcium by distillation from Downs cell sludge has been described.[93a]

It has also been proposed to dispose of the sludge by mixing it with material containing silica and heating in air to form sodium silicate, calcium oxide and silica.[93]

Patents have been taken out for the recovery of the calcium content of such sludges by treating them with an excess of an organic compound such as ethyl or methyl alcohol, which combines with both sodium and calcium but which initially reacts preferentially with substantially all the sodium to yield

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sodium ethoxide or methoxide which remains in solution. When the sodium is dissolved the sodium alkoxide solution can be filtered off before the calcium is appreciably attacked, and the residue dried to give calcium metal of 80–95% purity in a yield of 80–90%. The presence of small amounts of water in the alcohol is said to facilitate control of the reaction.[94,94b-e] Calcium has also been recovered by electrolysis of sludge in a monohydroxylhydrocarbon such as ethyl alcohol.[94a]

An apparatus has been patented for the safe disposal of Downs cell sludge by treating it in a column with an aqueous solution of the hydroxides of calcium and sodium.[95,96] The sludge is fed continuously at the bottom of the column, the subsequent reaction liberating hydrogen which keeps the system in violent agitation and continuously carries the metal to the top of the column, where a disengaging space is provided to separate the hydrogen from the strong hydroxide solution, which is removed in part, while the remainder of the solution is recycled. Weak hydroxide or water is added continuously at the bottom of the column.

Other Processes for the Manufacture of Sodium by Electrolysis of Fused Sodium Compounds.

In addition to the Castner, Ciba and Downs cells, a number of other cells for the production of sodium by electrolysis of fused sodium compounds have been patented. It has been proposed to withdraw the cell products separately in vapour or gaseous form.[50,97] It has been proposed to electrolyze fused sodium carbonate in a bath containing 64·4% of sodium carbonate and 35·6% of sodium chloride which melts at 600° C. The sodium chloride is not decomposed during the electrolysis which, may be carried out in a Castner cell.[98] A patent has been taken out for the production of sodium by electrolyzing a melt consisting chiefly of sodium borate in the presence of a molten alloy of sodium with tin or metals having similar properties, the alloy serving as the anode.[99] When sodium is prepared by the electrolysis of fused sodium nitrate, trouble arises owing to the migration of the nitrate ion from the anode compartment to the cathode compartment of the cell, where it reforms sodium nitrate by reaction with the metallic sodium liberated at the cathode, with consequent loss of cell efficiency. A process has been patented in which the electrolysis is carried out in the presence of sodium carbonate or sodamide, whereby migration of the anion is avoided, and its detrimental results suppressed.[100] These compounds react with the oxides of nitrogen liberated at the anode, producing gaseous carbon dioxide or ammonia which, being inert to the electrolyte, may be recovered together with the oxygen formed during the electrolysis. None of the foregoing processes seem to have met with any success on the technical scale.

PRODUCTION OF SODIUM ALLOYS BY ELECTROLYSIS

In spite of persistent efforts, the manufacture of sodium by the electrolysis of fused sodium chloride in the presence of a molten lead cathode never achieved any permanent success, and, since the advent of the Downs cell, has been regarded as obsolete. When sodium is utilized in the manufacture of tetraethyl lead, however, the metal must be in the form of a sodium lead alloy which has to be specially prepared from the metallic sodium. It is therefore possible that, for this purpose at least, an electrolytic route which produces a sodium-lead alloy in a single state may compete successfully with a two-stage process which involves making sodium in a Downs cell and then alloying it with lead, and it is interesting to note that such a development has occurred in Germany in recent years.

During the 1939-45 war a plant was erected at Heydebreck, Germany, by the I. G. Farbenindustrie for the manufacture of lead-sodium alloy by an electrolytic route developed by Hamprecht.[7,101]

The electrolysis was carried out using a graphite anode and a molten lead cathode with an electrolyte consisting of a mixture of sodium and potassium chlorides, melting about 700°C. The plant consisted of six cells each 2·5 metres wide and 4·5 metres long. The sodium chloride, previously melted in an electric furnace, was fed to the cells at the rate of approximately 50 kg. per cell per hour and a make-up of about 1·7 kg. of potassium chloride was also required. The cells were fed with approximately 160 kg. of lead per cell per hour and each cell produced approximately 4 metric tons per day of a lead-sodium alloy containing 10% of sodium, at a current efficiency of 80% and a voltage of 3·5 with an energy consumption of 8 kWh. per kg. of sodium. The chlorine produced by the cells was utilized in the production of ethyl chloride.

The lead-sodium alloy thus produced contained small amounts of potassium, and it is said that the presence of about 1% of potassium considerably increases the yield of tetraethyl lead obtained in the ethylation process.

It is claimed that the direct electrolytic production of a lead-sodium alloy for tetraethyl lead manufacture is economically advantageous and utilization of the alloy was confined to this purpose. Hamprecht showed that sodium hydroxide containing more than 99% NaOH could be made from the alloy, but no attempt appears to have been made to isolate metallic sodium. More recently the production of a sodium-lead alloy using a thin stream of molten lead as cathode in a cell for the electrolysis of fused salt has been developed by Szechtman.[101a,b] A cell for the manufacture of a sodium-lead alloy by electrolysis of fused sodium chloride has been described.[101c] A patent describes the preparation of sodium-lead alloys by the electrolysis of sodium chloride-sodium fluoride-potassium fluoride melts using a molten lead cathode.[101d] A sodium-lead alloy is produced by dissolving lead in sodium amalgam which has been prepared in an electrolytic cell with a mercury cathode, and then removing the mercury by distillation.[101e] Little further work appears to have been done on the preparation of sodium alloys by electrolysis. According to a patent an indium-sodium alloy may be prepared by the electrolysis of indium oxide in fused sodium hydroxide at about 425°C.[102]

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THE PURIFICATION OF SODIUM

Commercial grade Downs cell sodium attains the remarkable degree of purity of 99·95%,[1] and in the United States an even purer grade of metal is available.[2] Thus, commercial sodium is likely to be suitable for all ordinary laboratory purposes without further purification. There are, however, occasions, as for example when the sodium is required for determinations of the physical properties of the metal or for use as a liquid metal in a heat transfer system, when the presence of even traces of impurities may be deleterious. A considerable amount of work has accordingly been devoted to methods of purifying the metal.

One of the simplest methods of purifying sodium is by filtration.[1-6] The operation is carried out, preferably in an inert atmosphere, at a temperature at which the impurities in the sodium are in the solid state and the sodium itself is molten. It appears to be advantageous to allow the molten metal to age before filtration.[1]

Thus, in a method attributed to Bunsen, sodium is sealed under nitrogen in one compartment of a glass vessel divided into two compartments separated by a sieve. The sodium is heated in the first compartment till it has reacted with any water, oxygen or carbon dioxide in the nitrogen and is then filtered through the sieve into the second compartment, where it is allowed to solidify. The sieve retains any carbonate or hydroxide present in the sodium. The method is applicable to the purification of small amounts of sodium in the laboratory.[5]

It is stated that when molten sodium containing excess of sodium oxide is passed through a filter, which may be fabricated from sintered stainless steel or composed of several layers of fine-mesh stainless steel gauze, a filter cake consisting of sodium oxide is built up, and that continued cycling of the sodium through such a bed will finally give a filtered sodium almost completely free from oxide.[1]

Sodium oxide, carbonate and chloride are generally present in appreciable amounts in commercial sodium, and the extent to which these impurities can be removed by filtration obviously depends on their respective solubilities in the molten metal. Several laboratories have produced figures for the solubility of sodium oxide and sodium hydroxide in sodium and also in sodium-potassium alloys.[1,7a] Thus, the solubility of oxygen in sodium has been determined over the temperature range 130–540°C. and in sodium-potassium alloy over the range 20–176°C. using apparatus of both glass and stainless steel, and the sources of error encountered when using glass apparatus have also been investigated.[7] It is reported that the solubility of oxygen in sodium is 10 p.p.m. at 98°C. and 130 p.p.m. at 300°C.[8]

The solubility of sodium carbonate in molten sodium has been determined over the temperature range 150–385°C. The solubility is given as 0·002 and 0·027 wt.-% of sodium carbonate at 150° and 385°C. respectively.[8a] The apparent oxygen content (total alkalinity calculated as oxygen) of sodium saturated with sodium monoxide, sodium carbonate and sodium hydride for temperatures up to approximately 400°C. has also been determined and is found to be low at temperatures just above the melting point of sodium.[11b]

Sodium hydride is another impurity which is likely to be present in unpurified sodium. Solubility determinations show that the solubility of the hydride is 4·29 wt.-% of sodium hydride at 445°C. and falls to 0·005 wt.-% at 250°C.[8a,11d] Removal of sodium hydride by filtration should therefore be feasible.

The following figures are given for the solubility of sodium chloride in molten sodium.[9]

Temperature °C.	Mole % Sodium Chloride in Molten Sodium
550	0·12

continued on following page.

Temperature °C.	Mole % Sodium Chloride in Molten Sodium
750	1·8
781	2·2
790	2·9
832	4·2
874	5·8

No determinations appear to have been carried out at lower temperatures, but the above results suggest that the solubility falls off rapidly with decreasing temperature and that the amount of sodium chloride in solution in molten sodium at temperatures slightly above the melting point of the metal is likely to be very small.

Sintered stainless steel filters with a nominal pore size of 5–10 microns have been found satisfactory for the purification of sodium by filtration.[2]

An apparatus for the filtration of sodium has been patented.[10a]

In the studies of surface properties of liquid sodium, as for example surface tension and contact angle, it is essential to maintain a perfectly clean surface on the molten metal for long periods of time and this involves the use of an inert gas atmosphere of high purity. Molten sodium surfaces are highly sensitive to traces of moisture and readily become clouded in the presence of this impurity. When using an inert gas atmosphere of argon dried first by magnesium perchlorate and then by phosphorus pentoxide it was found that a molten sodium surface clouded over in 1 hr., whereas when the argon was purified by passing it through a molecular sieve, the surface of the metal remained bright indefinitely. The effect of the molecular sieve is attributed to the removal of moisture from the argon, and not to the removal of oxygen.[11a]

Molten sodium may be freed from oxygen-containing sodium compounds such as the oxide or hydroxide by a process that has been called 'gettering' by analogy with the removal of oxygen and other gases in vacuum technology.[1,10] This consists in adding to the molten sodium substances which reduce the sodium oxides to sodium metal, and at the same time form an oxygen-containing compound insoluble in molten sodium. It is essential to heat the mixture of sodium and the getter to such a temperature that reaction between the oxide and the getter will take place. When the reaction is completed, the molten sodium is cooled to a temperature just above its melting point and then filtered to remove the insoluble compound formed by the gettering process, thus giving a filtrate of oxygen-free sodium. Magnesium and calcium have been recommended as gettering materials.[1,10] The oxygen content of a sample of calcium gettered sodium has been given as probably less than 0·005 wt.-%.[10]

A cold trap on the system might be expected to remove getter oxides, but no information appears to be available on the performance of cold traps in this way.[11b] A second class of gettering agents consists of those which are themselves essentially insoluble in sodium or sodium–potassium alloy and which reduce sodium oxides to the getter oxide which is also insoluble in the molten metal. Materials used in this way are titanium, zirconium and uranium.[11b-m] In practice the getter material in massive form is supported mechanically in the stream of molten metal and the getter oxide forms on the surface of the getter. A very heavy coating of oxide may lead to flake off and be carried round the system and settle out at a low point with consequent danger of blockage. There is no evidence that the chromium in stainless steel lowers the oxygen content of molten sodium significantly, although it is stated that some reduction of oxide by chromium does take place.[11b]

Small amounts of potassium can be removed from molten sodium by digestion with graphite at 300°C., followed by filtration. The lower limit of potassium removal in this way is 30 p.p.m.[11b]

According to a patent, sodium containing small amounts of an alkaline earth metal such as calcium can be purified by subjecting it in the molten state to the action of an oxidizing agent such as air or sodium hydroxide at a temperature not less than 350° C. The alkaline earth metal is converted into the oxide, which may then be separated from the molten sodium by filtration or other means.[11] The purification of sodium containing larger amounts of calcium has already been discussed. (see page 352).

The removal of impurities from molten sodium and sodium-potassium alloys by the use of a cold trap has recently found extensive application in heat transfer systems.[11c-m]

Cold trapping is essentially a method of removal of impurities based on the solubility-temperature relationship, and in its simplest form consists of a surface on which precipitation takes place by virtue of its being colder than the saturation temperature of the impurity.[11c]

Cold traps may be classified as natural and forced circulation traps. A natural circulation trap can be merely a cold steel end somewhere in the system, although it is generally a vessel with means of draining. Delivery of impurities of the circulating stream of molten metal to the cold surface of the trap is dependent on natural circulation brought about by turbulence at the entrance of the trap, and diffusion of the impurities into the trap. In the forced circulation trap, a portion of the circulation metal (generally 1–2%) is by-passed and pumped over a cold surface, thus giving more intimate and rapid mixing than is possible with a natural circulation trap. A typical cold trap operates at a temperature of about 150° C. with a main stream temperature of about 250° C.[11c]

The basic function of the cold trap in heat transfer systems is to remove sodium oxides, and vessels packed with stainless steel wool or stainless steel mesh will give an exit stream with an oxide content closely approaching the solubility of the oxide at the cold trap temperature. Ordinary steel work is not satisfactory and tends to break up.[11c]

In addition to oxides, materials which have a sharply changing temperature solubility in sodium such as antimony and silver are also removed. Metallic impurities such as iron, chromium, cobalt and nickel also appear in cold traps in some quantity.

The mechanism of the transport of these impurities has not, however, been determined.[11c]

The removal of hydrogen as sodium hydride from molten sodium by means of cold trapping has been demonstrated.[11d]

The impurities deposited in the cold trap can be returned to the main stream by heating the trap and the oxygen content of the circulating metal can be maintained at any desired level by adjusting the cold trap temperature. The design and performance of cold traps has been discussed.[11c-h]

Oxide solubility variation with temperature is also made use of in the plugging indicator, a device for measuring the oxide content of liquid sodium and sodium potassium alloys systems in a semi-continuous manner without removing samples from the system. A portion of the main stream is directed through a by-pass loop containing a cooling jacket, an orifice plate and a flowmeter. In operation the temperature of the by-pass stream is successively reduced by increasing the coolant flow until it falls slightly below the value corresponding to saturation of the liquid with oxide. At this point, solid oxide precipitates out, plugging the orifice and thus reducing the by-pass flow as indicated on the flowmeter. By noting the temperature at which this takes place, the saturation limit, and hence the oxide content, of the liquid can be determined.[11i] Plugging can however also result from other insolubles such as metal chips, weld slag, calcium oxide and residues produced by the reaction of sodium with hydrocarbons, and to obtain accurate oxide determinations these impurities must be absent.[11d]

The purification of sodium by distillation has been studied.[1,12-16] It is said that most of the impurities in sodium, with the exception of sodium oxide, can be removed by distillation, which may be carried out in glassware under reduced pressure,[1] or in metal equipment at normal pressures.[1] It may be desirable to reject the light and heavy fractions of the distillate.[14] The following analysis has been given for vacuum-distilled sodium: sodium 99·995%, boron 40 p.p.m., potassium 20 p.p.m., oxygen 5–10 p.p.m.[15] A simplified procedure for the simultaneous preparation of several samples of twice distilled sodium in Pyrex glass ampoules has been described and it is claimed that the product is entirely free from oxide or other contaminants.[16] There seems, however, to be some doubt as to the extent to which sodium oxide can be removed by distillation. Thus, it is claimed that experiments with irradiated sodium oxide have shown that no trace of sodium oxide distils at 600°C. in vacuo:[17] on the other hand it is stated that the oxygen content of triple-distilled sodium is 0·008 ± 0·003%.[18] Another author gives the oxygen content of distilled sodium as 0·0005–0·0010%.[15]

The iron content of double-distilled sodium is stated to be very similar to that of triple-distilled sodium: colorimetric determinations give the iron content of the latter as 1 part in 8×10^6 parts of sodium.[19]

The rates of reaction with air of filtered and distilled sodium have been compared.[19a]

One patent describes a glass which resists sodium vapour and therefore might by suitable as a constructional material for sodium distillation apparatus.[20]

The feasibility of sodium purification by distillation is discussed. It is concluded that sodium chloride and sodium sulphite can be separated by distillation at 450°C. Magnesium is not likely to be completely eliminated by distillation. The vapour pressures of manganese, silver, aluminium, beryllium, copper, nickel, iron and boron favour quantitative retention in the undistilled residue. Some doubt appears however to exist regarding the possibility of completely eliminating calcium and silicon by distillation.[20a] A combined filtration and vacuum distillation unit for the purification of sodium has been described. Operating data are given.[20b]

Sodium containing mercury may be purified by passing it in the molten condition over calcium at 380°C.[6]

Other methods of purification have been suggested. It is claimed that sodium can be purified by melting it repeatedly in contact with petroleum.[21] Patents describe the purification of sodium by heating it in a steel tube in contact with sodium chloride or other inert salts.[22,23] Another patent describes a process for the purification of sodium whereby the metal is dissolved in liquid ammonia, the solution filtered to remove the undissolved impurities, and the sodium recovered by removing the ammonia by evaporation.[24]

FORMS OF SODIUM

Sodium may be conveniently handled and applied in the form of dispersions.[25-27b] In systems in which sodium is insoluble, reaction takes place only at the sodium surface and the rate of reaction is a direct function of the surface available. By the use of dispersing agents, molten sodium can be emulsified in inert liquids, and a large surface area thus made available. It is frequently found that surface films of insoluble reaction products build up on a sodium surface and tend to isolate it from further access to reagents. When small particles of sodium are used, a point is reached, in the 1 to 10 micron particle size range, when reaction of the sodium is complete before the inert film is thick enough to hinder reaction seriously. Techniques for producing dispersions of sodium in inert liquids have been described.[25-27h]

Sodium in the form of a dispersion in petroleum jelly is prepared by heating a mixture of the two ingredients, normally containing from 10–30% of the metal, to a temperature at which both components are fluid and then subjecting the mass to violent agitation while cooling. The petroleum jelly protects the metal so well that the dispersion may be immersed in cold water without any apparent evolution of hydrogen taking place.[27i]

More recently sodium has been produced in the form of 'high-surface' sodium.[28] This term is applied to films of sodium approaching colloidal dimensions spread over inert solids of high surface area to give a free flowing product. It is claimed that sodium in this form is advantageous for the preparation of finely divided metals, for the purification of hydrocarbons and ethers and for the preparation of inorganic and organic derivatives. In these applications high-surface sodium affords easy control of reaction rates at temperatures below and above the melting point of sodium, and also eliminates the risks attending the use of inflammable dispersion materials. It is also claimed that induction periods are reduced or eliminated, and that the products may be prepared in a finely divided and highly reactive state. In addition, yields are high, and the use of high-surface sodium lends itself to continuous operation. The following solid carrier materials have been used in a finely divided form for the preparation of high-surface sodium:-

1. Activated alumina
2. Activated coconut carbon
3. Iron powder
4. Colloidal carbon
5. Sodium chloride
6. White sand
7. Sodium carbonate
8. Zirconium oxide

The amount of sodium that can be absorbed while maintaining the carrier material as a free flowing product depends on the total surface area of the solid carrier. Thus, salt may carry from 2–10%, soda ash 10% and alumina 20–25% of sodium. In the case of activated or colloidal carbons, however, the sodium content may exceed 30%. The free flowing characteristics can be maintained at temperatures up to the boiling point of sodium, provided that the carrier remains stable at such temperatures.

The reactivity of high-surface sodium systems with air and water have been studied.[28] Sodium–carbon systems become heated to redness on exposure to air owing to the oxidation of the sodium and the carbon; other carriers for sodium which are combustible, such as finely divided metals, may ignite. On the other hand sodium dispersed on non-inflammable carriers such as alumina, salt, soda ash etc. becomes heated on exposure to the atmosphere but does not ignite, and frequently such systems are found to react with water in a comparatively gentle manner with only a rapid evolution of hydrogen which does not ignite or explode. The preparation of high-surface sodium, and a number of its applications, have been described in detail.[28]

The preparation of colloidal sodium has been described.[28a-c]

Sodium is also available in the form of spheres about 0·2 to 2 mm. in diameter, generally termed sodium sand.[29] This product, made by shaking or stirring molten sodium in an inert hydrocarbon oil, provides a convenient means of introducing sodium into reaction zones in definite amounts.[29] Metal in the form of slightly larger spheres of 0·5 to 1·0 in. diameter is also available, and is termed 'sodium marbles'.[30] One patent describes the production of sodium in the form of an extruded continuous core, small and substantially uniform in cross section, enveloped by a thin continuous tightly fitting sheath of another metal resistant to oxidation, such as lead. The sheath may be crimped at the ends to seal the core from the atmosphere.[31]

Sodium may also be prepared in a subdivided form by grinding the metal in an inert atmosphere at temperatures below 0°C., and preferably below -90°C.[32]

A highly pure form of sodium, described as 'Argon grade' sodium, has recently become available in the United States.[2,33] This material, which is filtered and packed under an atmosphere of argon, is said to be free from oxygen or nitrogen, and is recommended for use where traces of such gases are considered to be deleterious.

A new reactor-grade sodium which contains less than 25 p.p.m. of calcium has recently become available, and is now being used in atomic power systems in America.[33a]

HANDLING, STORAGE AND AVAILABILITY OF SODIUM

The handling and storage of sodium has been dealt with by a number of authors.[34-41i] Among the subjects discussed in detail are fire prevention and fire fighting, cleaning of contaminated apparatus and equipment, disposal of waste sodium residues and protective clothing for personnel handling sodium. A safe technique for handling sticks of sodium on a large scale has also been described.[40] In general it may be said that the safety precautions desirable with sodium are well known and need not be considered further here. Attention is, however, drawn specifically to the following hazards, the significance of which did not appear to be appreciated when the original Treatise was published.

Sodium and the other alkali metals form detonating mixtures with organic halogen compounds and also with solid carbon dioxide and on this account carbon tetrachloride must not be used to put out sodium fires.[41,42] Such fires are best dealt with by smothering them with dry sand, or better with dry soda ash or salt. Sodium bicarbonate must not be used in place of soda ash.[1,41] The use of a mixture containing 704 parts of sodium chloride, 20 parts of pitch and 16 parts of graphite for extinguishing sodium fires has been patented.[43] Other alkali or alkaline earth metal chlorides may be used in place of sodium chloride.

Dangerous mixtures are formed by the partial oxidation of sodium. Thus, when molten sodium is exposed to air, the surface of the metal rapidly becomes coated with a film of oxide or hydroxide, and as the oxidation proceeds this film becomes a viscous mixture of metallic sodium with oxidized sodium compounds.[41] This mixture tends to ignite easily and is dangerous. Similarly pieces of dry sodium exposed to air for a period may acquire a film which should be removed with a knife before returning the metal to an enclosed space, since the film reacts slowly with sodium metal evolving hydrogen which may give rise to fire or explosion.[41] Data on the flammability of sodium alloys at 600–800° C. are available.[42a,b]

The disposal of sodium wastes and residues has also been investigated. A novel method for the safe and rapid disposal of large quantities of sodium has been described.[44,44a] Molten sodium at 350° F. is discharged under a minimum depth of 10 ft. of water through an annular orifice with a free area of 0·226 sq. in., at flow rates of approximately 90 lb. per minute. The hydrogen produced by the reaction does not ignite, and little sodium oxide smoke is formed. Sodium detonates with great violence when thrown on ice.[44b]

Liquid ammonia and ammonia–ammonium chloride washes are effective for removing sodium and sodium sludges from a liquid metal system.[44d] Cleaning has also been accomplished by the use of a mixture of water vapour and inert gas.[44c]

The fire and health hazards of radioactive sodium include all those mentioned for ordinary sodium with an additional radiation hazard. When sodium is used as a reactor coolant, radioactive ^{24}Na tends to build up to an equilibrium value, and this is a very powerful beta and gamma emitter having a half life of 14·8 hr. The known hazards of this isotope have been classified, and design of equipment of systems producing the isotope, protective clothing, fire fighting, first aid equipment, disposal of radioactive sodium waste, and regulations governing shipping of radioactive sodium in U.S.A. have been discussed.[44e]

A precision sodium cutter has been described.[45]

An account of the resistance of materials to corrosion by liquid sodium over a wide temperature range is given.[46-46z] Static corrosion tests at temperatures between 400° and 500° C. for a period of 1 month, using sodium with a probable oxygen content of 0·005–0·01%, show excellent corrosion resistance for Armco iron, beryllium, nickel, Monel metal, numerous stainless steels and zirconium. In the case of aluminium and many aluminium alloys resistance is poor, but that of aluminium bronze is excellent. Steels are quite satisfactory over longer periods. Thus, liquid sodium has been transferred continuously for many years in a mild steel pipe without any sign of deleterious attack on the pipe wall, and clean liquid sodium has been handled in stainless steel at 500°C. for periods up to three years without failure of the container. Static corrosion tests have also been carried out using calcium 'gettered' sodium with a probable oxygen content of less than 0·005%. The corrosion of iron by sodium contaminated with oxygen has been investigated.[46s] The mechanism of liquid sodium corrosion has been discussed and is said to be largely a solution phenomenon.[47] The effect of impurities, temperature, temperature gradient and flow velocity on corrosion mechanism have been studied.[47-47c] Non-metallic materials such as beryllia, zirconia, magnesia, alumina, molybdenum disilicide and numerous metal-ceramics are not attacked by sodium when they are in a sufficiently dense form, but are penetrated and disintegrated if porous.[46] The corrosion of molybdenum wire at 1500°C. in sodium vapour has been studied.[48]

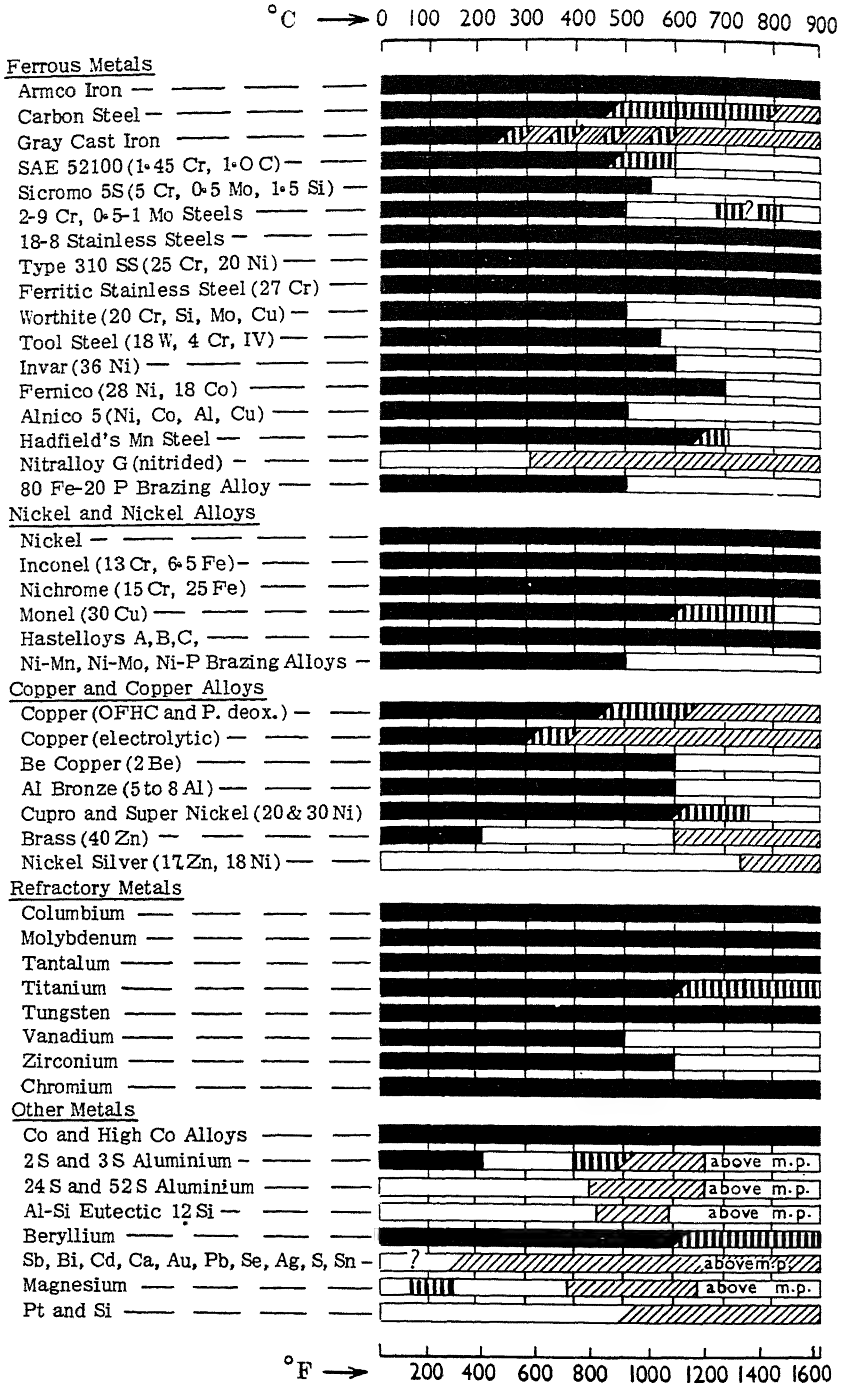
Sodium does not react with glass at temperatures below 300°C., but above this temperature Pyrex glass is rapidly attacked.[46] Extensive tests have been carried out to determine the protective qualities of various items of safety equipment in contact with hot sodium.[49]

The handling of sodium in molten form in heat transfer systems has been described, and information is available on the pumping of liquid sodium by means of mechanical and electromagnetic pumps.[49-54i] A novel pump for the continuous feeding of sodium at metered rates has also been described.[54]

The handling and storage of sodium–potassium alloys are discussed under Potassium (see Suppl. 3).

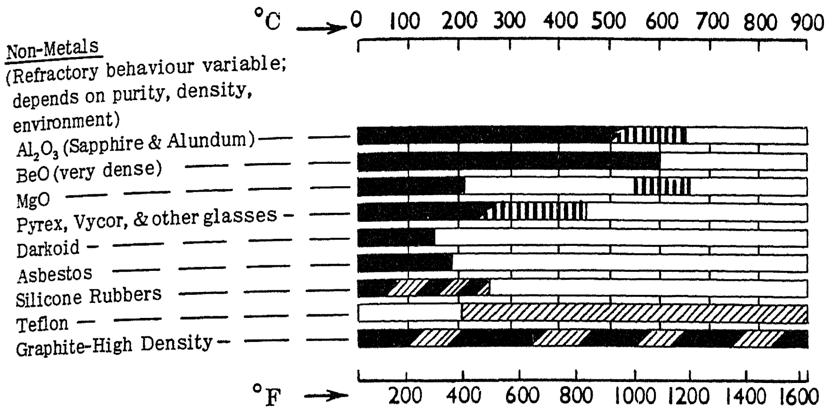
For large scale industrial use in Great Britain, sodium is generally cast in the form of blocks weighing $12\frac{1}{2}$–15 lb. A process for the continuous casting of sodium has been patented.[54j] There is also a considerable tonnage of $3\frac{1}{2}$ lb. blocks, pellets and sticks, and the metal is generally shipped in airtight containers in preference to the older practice of shipping under naphtha.[55] In the United States sodium is also shipped in rail tanks.[37] The tank car used has a capacity of 40 tons and is equipped with pipes welded to the inner shell for circulating heating or cooling oil between the inner and outer shells. As the tank is being filled with sodium under an

TABLE VII.- RESISTANCE OF MATERIALS TO LIQUID SODIUM AND SODIUM POTASSIUM ALLOYS[46]



continued on following page

TABLE VII. continued



Resistance Ratings.

(These ratings refer to liquid-metal resistance only–not to temperature-dependent mechanical strength or metallurgical stability. See text for further discussion.)

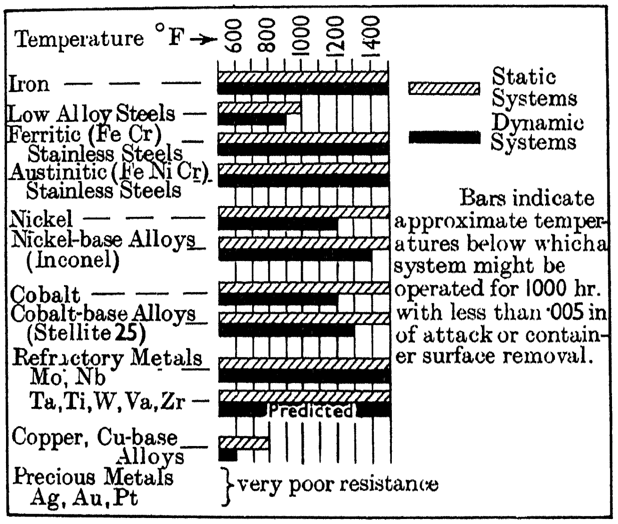
■ – GOOD Consider for long-time use.

▥ – LIMITED Short-time use only.

▨ – POOR No structural possibilities.

☐ – UNKNOWN Information inadequate.

TABLE VIII.- CORROSION RESISTANCE OF VARIOUS METALS AND ALLOYS IN SODIUM COMPOSING STATIC AND DYNAMIC SYSTEMS



inert atmosphere of nitrogen, cooling oil is circulated through the system, thus solidifying the sodium: when filled the tank is sealed under nitrogen. When the tank arrives at its destination, the sodium is remelted by circulating heated oil and the molten metal is withdrawn by applying a vacuum to the unloading line and adding nitrogen to the tank as emptying proceeds. The low melting point, low specific gravity, high heat conductivity of sodium and the large scale demand for the metal make this shipping practice feasible, and this is probably the only case in which a metal is shipped in such a manner.

The storage of sodium in capillary tubes has been described in a number of patents.[56,57]

No adhesion occurs between sodium and polythene, and metal encased in that material may be stored without deterioration.[57a] A ferrous metal container for sodium, having a phosphatized inner surface which prevents adhesion of sodium to the container walls, has been patented.[57b]

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THE USES OF SODIUM

In the year 1888, H. Y. Castner started to manufacture sodium on the commercial scale at Oldbury, England, using a modified form of Deville's process.[1] The product was utilized in an adjacent plant for the manufacture of aluminium by the reduction of aluminium chloride. This new route to aluminium resulted in a substantial reduction in the price of that metal, and the Castner plant ran successfully for over two years, during which it produced over one hundred tons of aluminium. The process had scarcely become

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established, however, when the introduction of the present electrolytic method of aluminium manufacture rendered the use of sodium for this purpose unnecessary, and this greatly reduced the demand for the latter metal. Thus, Castner, who at that time had recently developed a cell for the manufacture of sodium by the electrolysis of fused sodium hydroxide, found himself with a process for making sodium but no market for his product. The future prospects for sodium must have seemed very black indeed, but Castner lost no time in turning his attention to other possible uses for the metal, and it is no small tribute to the inventive genius of that remarkable man, that he very quickly succeeded in developing two new outlets for sodium, based on the manufacture of sodium cyanide and sodium peroxide. As might well be expected a number of further uses for the metal have been developed since then, notably in the manufacture of tetraethyl lead and alkyl sulphates, but substantial amounts of sodium still continue to be used in cyanide and peroxide manufacture.

The following figures are given for the amounts of sodium consumed by various usages in the United States:-

Use	Million pounds per year		
	1947[2]	1948[2]	1953[3]
Tetraethyl lead	66	90	137
Sodium cyanide	25	32	40–50
Sodium alkyl sulphate	25	32	50
Sodium peroxide	7	7	7–10
Sodium hydride	2	2	–*
Indigo synthesis	2	2	–*
Miscellaneous	6	6	–*
	133	139	–*

* No figures available

No comparable figures have been given for other countries or for world usage.

It will be appreciated that in addition to the major uses listed above the heading 'miscellaneous' covers a very large number of comparatively minor applications of the metal, so that it is not possible here to do more than survey this field in a general manner. For further information on this subject the reader is referred to chemical encyclopaedias such as Kirk Othmer[4] and Thorpe,[5] and also to the numerous reviews which have been published on the uses of sodium.[1-3,6-16m]

The production of sodium cyanide still represents one of the major outlets for sodium. Sodium cyanide is manufactured by reaction of sodium with ammonia to yield sodamide, which then reacts with carbon to give sodium cyanamide. The cyanamide reacts in turn with additional carbon to form sodium cyanide: $2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$; $2NaNH_2 + C \rightarrow Na_2CN_2 + 2H_2$; $Na_2CN_2 + C \rightarrow 2NaCN$. Among the important industrial applications of sodium cyanide are gold extraction,[12] electroplating,[12] case hardening,[12] hydrocyanic acid manufacture[12] and organic syntheses.[12] Sodium peroxide is manufactured by burning sodium in air under carefully controlled conditions.[13] It is a powerful oxidizing agent and is used principally in the bleaching industry as such, and also in the manufacture of bleaching agents such as sodium perborate or percarbonate.[12]

The largest single use for sodium metal is in the manufacture of tetraethyl lead, used as an antiknock compound in petrol,[14] by reaction of a lead-sodium alloy with ethyl chloride according to the equation:-[12]

$$4PbNa + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl.$$

The utilization of sodium in the preparation of tetraethyl lead is responsible for the very large expansion in the demand for the metal during the last thirty years. The advent of the jet engine, which does not use tetraethyl fuels, may have a profound effect on the demand for sodium.[1] Similarly the Ziegler route to tetraethyl lead, which does not use sodium, has threatened the applications for the metal.[18]

The growth of the synthetic detergent industry has resulted in an increasing demand for large quantities of fatty alcohols.[15,15a] These are prepared by the sodium reduction of the higher fatty acid esters in the presence of a suitable alcohol. Thus, in one process triglycerides are reduced with sodium in the presence of 4-methyl-2-pentanol to yield the sodium salt of the fatty alcohol, which is then hydrolyzed to yield the alcohol and caustic soda. The sodium salt of the sulphonated alcohol is used as a detergent.[15]

Sodium hydride is formed by the reaction of molten sodium with hydrogen at 250–300°C. and can be substituted for sodium in many organic reactions. In recent years a substantial amount of sodium has been used in the preparation of sodium hydride for the descaling and deoxidizing of steels.[17,18] The hydride is prepared by dissolving sodium in a bath of fused caustic soda in the presence of hydrogen, and this gives a bath having a number of advantages over the conventional aqueous acid baths used for pickling. Thus, for example, the sodium hydride process eliminates pitting, hydrogen embrittlement and loss of metal, all of which are objectionable features in acid pickling.

An important outlet for sodium lies in the production of dyes and dyestuffs intermediates. In the synthesis of indigo, the sodium or potassium derivative of phenylglycine is fused with sodium hydroxide or potassium hydroxide, or a mixture of these hydroxides, in the presence of sodamide or sodium. The fusion product, indoxyl, is then hydrolyzed in water and oxidized with air to yield indigo.[19] Sodium may be used in the condensation of ethyl acetate with ethyl oxalate to form ethyl oxalacetate, a raw material used in the manufacture of pyrazolone dyes.[20] The intermediates of the Hansa group of dyes are formed by the condensation of acetoacetic ester, which may be made by reaction of ethyl acetate and sodium, and an amino compound.[12] The metal is also used extensively in the preparation of drugs such as sulphapyridine,[21] sulphamerazine,[21] barbiturates,[22] antipyrine and antimalarials.[12]

Sodium is also used in the synthesis of perfumes. Thus, for example, phenylethyl alcohol, which has an odour of roses, is prepared by the reduction of phenylacetaldehyde with sodium.[12]

Liquid ammonia is an excellent solvent for sodium and solutions of sodium in that medium have been extensively employed for organic reductions.[23-25b] It is suggested that the reduction of hydrocarbons by sodium in liquid ammonia is probably dependent on the addition of the metal at the double bond.[24] Among the reductions which have been carried out in this manner are those of acetylenes to olefines,[26] of phenanthrene to 1:2:3:4-tetrahydrophenanthrene[27] and of benzyl alcohol to toluene.[28]

A number of patents have been filed on the purification of hydrocarbons with sodium or sodium alloys.[29-35] This method of treatment has been applied to vapours from hydrocarbon materials such as cracked distillates,[29] to refined lubricating or other hydrocarbon oils[32] and to hydrocarbons such as indene, butadiene, styrene or piperylene,[33,34] and naphthalene.[35] It has also been proposed to purify hydrocarbon vapours by electrolyzing fused sodium chloride to give a mixture of sodium and sodium chloride which is then brought into contact with the vaporous hydrocarbon material and subsequently recycled

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to the zone of electrolysis.[36] Sodium is also employed in the polymerization of unsaturated hydrocarbons,[37-37m] and in alkylating and condensing aromatic hydrocarbons.[37k,37l] Comprehensive reviews which describe the uses of sodium in organic chemistry are available.[39b-m]

It is claimed that many of the technical difficulties encountered in the application of sodium to the refining of hydrocarbons have been overcome by the use of sodium dispersions in liquid media.[38] Such refining operations may also be carried out with colloidal sodium adsorbed on inert solids, generally termed high-surface sodium.[39] Thus, sodium dispersions have been used to remove sulphur compounds, including thiophen, from petroleum.[38]

The purification of crude titanium tetrachloride is carried out by distilling the material in the presence of a sodium–lead alloy.[40] The alloy is added to the crude tetrachloride in a concentration of 4–30 parts per 1000 parts of tetrachloride. The vanadium content of the tetrachloride is thus reduced from 0·15% to 0·002% or less.

In recent years the application of liquid metals as high temperature heat-transfer fluids has been the subject of much research and development work.[41,42c] Liquid sodium has many advantages as a heat transfer medium. It has a very high heat transfer coefficient, a low melting point and a high boiling point, does not decompose or polymerize on heating, and in the absence of oxygen or moisture does not attack iron or steel.[41,42] During the 1939–45 war, heat transfer systems using sodium were operated in the United States on a technical scale, one such installation having a capacity of 1,500,000 B.Th.U. per hour.[41] Experimental liquid metal heat-transfer systems using sodium or sodium alloys are discussed in detail by Trocki.[42]

The excellent heat-transfer properties of molten sodium are also utilized in a number of other ways. For example, the valves of some internal combustion engines are cooled by the use of sodium in the hollow stem and head of the valve. The sodium, which is liquid at the working temperature of the valves, is very effective in reducing the temperature of the valve head and the surface in contact with the valve seat, by dissipating heat via the stem. These valves are extensively employed in modern aircraft engines and also in heavy duty buses and trucks.[41,43,44] Sodium is also used as a coolant in the agitator arms used to move shale heated in a retort in order to recover its oil content.[45] In casting magnesium, sodium-filled cores are utilized to facilitate heat dissipation[41] and sodium–potassium alloy baths are used in heat treatment furnaces.[41] The possibility of using sodium–potassium alloys as coolants for vacuum arc melting furnaces in the production of titanium ingots has been examined.[46a]

Sodium is a good conductor of electricity and has been used for this purpose in place of copper. An installation consisting of an iron pipe filled with sodium, with a capacity of 4000 amp., has operated satisfactorily for a period of several years.[46] The weight per unit conductivity was found to be decidedly less than for copper, and when the experiment was carried out in 1930, the cost per running foot of conductor was approximately the same for copper and for a sodium pipe conductor. It was suggested that the use of sodium as a conductor should be limited to permanent installations where high currents at relatively low voltages are transmitted.

There are extensive uses for sodium in the metallurgical field. Thus, the metal is used, generally in the form of an alloy, for the deoxidation of heavy metals such as copper,[47] brass,[48] bronze[47] and iron.[49,49a] It is also employed to modify the structure of aluminium alloys high in silicon, with resultant improvement in mechanical properties.[50-53l] Lead containing small amounts of sodium is used as a bearing alloy with good frictional properties,[54,55] and sodium is employed for the removal of antimony and bismuth in lead purifica-

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tion.[56] Sodium has been used to improve the properties of cast iron.[56a, b]

In the purification of heavy metals such as iron, it is convenient to add the sodium in the form of a dispersion in a carbonaceous liquid such as kerosene.[57] The dispersion is directed against the molten metal surface through a small orifice from a container by means of nitrogen pressure. The kerosene burns, but it is claimed that the addition of sodium in this manner is less hazardous than any other common method of addition.

It is said that the addition of sodium to mercury for use in the amalgamation of gold ores improves the recovery of gold, and a similar addition is recommended for increasing the efficiency of extraction of platinum from platinum ores with mercury.[58] The effect is attributed to the lowering of the surface tension of the mercury by the sodium, which thus increases the tendency of the mercury to wet the precious metals in the ores.[12] This lowering of surface tension also underlies a suggestion that alloys of tin or zinc containing small amounts of sodium are advantageous in promoting thin coatings of sheet iron with tin or zinc.[12,59,60]

A zinc–sodium alloy has been proposed for use in electroplating zinc from zinc cyanide.[61]

In view of the early history of the production of sodium (see page 368) it is interesting to note that in recent years the preparation of metals such as calcium,[61a, b] zirconium,[62,62a] titanium,[63-72c] beryllium and tantalum,[73,74] vanadium and chromium[75] by the reduction of their compounds with sodium has been investigated, and in at least one case, namely that of titanium, apparently with considerable success. According to recent information, the preparation of titanium by the reduction of titanium tetrachloride with sodium has now been adopted on the commercial scale in England[65] and America[70] and this process will be dealt with in a later Supplement. The 'Argon grade' sodium available on the market in the U.S.A. is recommended for use in the preparation of metals such as titanium or zirconium.[76] Boron and silicon have also been produced by the reduction of their respective chlorides with sodium.[76a, b]

Many metal salts and oxides react smoothly with sodium absorbed on inert carriers. Such reactions proceed rapidly and completely at relatively low temperatures, and the metals so produced are colloidal and therefore in an extremely reactive form, which for some purposes may be very advantageous.[77] Examples of metallic compounds that have been reduced in this way include lead chloride, copper chloride, nickel chloride, silicon tetrachloride, titanium tetrachloride, zirconium tetrachloride, chloroplatinic acid, iron oxide, zinc oxide and metal soaps such as nickel oleate.[39]

A patent describes the preparation of powdered metals at low temperatures using sodium dispersed in toluene or ether.[39a]

The preparation of metallic powders by reducing a metallic compound with a sodium metal addition-compound of ethers of polyhydric alcohols such as glycol ether, has been patented.[78-78b] The sodium addition-compound is conveniently prepared by causing the ether of a polyhydric alcohol to react with metallic sodium in a subdivided state e.g. as a dispersion of sodium in an inert liquid medium. The method has been used to produce powders of iron, cobalt, chromium, manganese, molybdenum, zinc, tin and silver. Powder alloys of iron–cobalt and iron–chromium as well as other mixtures of different metal powders are prepared in a similar manner.

An interesting minor application is that of improving the effectiveness of automobile lubricating oils. A sodium 'slug' in a special fitting in the oil feed line greatly increases the useful life of the oil, perhaps by removing, or preventing, formation of the deleterious oxidation products which are mainly responsible for the deterioration of lubricating oils.[89] Leaks in pipes are studied by watching the movement of a slug of sodium, ^{24}Na.[90]

23.6

Sodium finds many other minor uses in the purification of gases,[79,80] the manufacture of photoelectric cells[81-85] and in sodium vapour lamps.[86] A liquid sodium pump for removal of oxidizing gases from inert atmospheres has been described.[86a] A 25% sodium-lead alloy (Hydrone) is used to generate hydrogen,[12] and a floating marine flare containing metallic sodium and light hydrocarbon has been patented.[87] Small quantities of sodium are employed in the manufacture of sodium azide which is used to make primers for percussion caps.[88]

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SECTION XXIV

THE PHYSICAL PROPERTIES OF SODIUM

By W. H. WILSON

Structure, Atomic and Ionic Radii, Etc.

While the silvery-white surface of freshly-cut sodium tarnishes almost instantaneously in air, surfaces cut under liquid nitrogen remain bright for several hours at -196°C. even though no special precautions are taken to prevent precipitation in the liquid nitrogen of ice from the moisture of the air.[1] Sodium can be polished metallographically in the same way as can lithium (see page 31) but by using propyl alcohol instead of methyl alcohol.[2] Brilliantly lustrous dodecahedra of sodium have been obtained by the slow evaporation of a liquid ammonia solution of the metal.[3]

Single crystals of sodium may be prepared by allowing the liquid metal to cool very slowly in oiled tubes.[4-6] Basically similar techniques for doing this have been devised independently by Andrade and Tsien[4] and by Quimby and Siegel.[5] The former workers contained the sodium in a tube 13 cm. long and 2 mm. in diameter, and this was lowered at a rate of 12 cm. per hour from a jacket maintained at 100°C. Quimby and Siegel lowered the containing tube from a heated zone at a rate of 5 cm. per hour and obtained crystals with a diameter of 4·7 mm. which were single over their entire length of 10 cm. The crystals showed no tendency to grow in any preferred orientation.

Sodium crystallizes as a body-centred cube, the most precise value for the lattice constant being 4·2820 ± 0·0005 A. at 20°C.[7] This corresponds to an atomic radius of 1·85 A. Other values of 4·27 A.,[8] 4·29 A.[9] and 4·30 A.[10] have been reported for the lattice constant at ordinary temperatures. The body-centred cubic lattice still holds at 90° to 100°K. where the lattice constant is 4·24 A.[11,12]

There is evidence of a transformation to a face-centred cubic structure in sodium that has been cold worked at liquid hydrogen temperature and then *X*-rayed at -195°C.[13] This strain-produced modification may be likened to that found in cold worked lithium at liquid nitrogen temperatures (see page 32). The lattice constant of the face-centred cubic form is 5·339 A. at -195°C., and the densities of the two forms are almost identical.[14] More recently, Barrett[15] has sought and found in sodium at very low temperatures a spontaneous martensitic transformation analogous to the spontaneous transformation to a hexagonal close-packed structure found previously in lithium at low temperatures (see page 32). Specimens of sodium were cooled to various low temperatures and then examined metallographically near room temperature: martensitic transformations were detected by the scars left on the specimens as a result of the plastic flow that occurs. Large unrestrained grains of sodium (99·94% pure), free from oxide, were found to undergo a partial martensitic transformation when cooled below 36·2 ± 2°K. Smaller grains with unoxidized surfaces usually began to transform at about 31°K., whereas those with oxidized surfaces transformed at rather lower temperatures. On cooling to 25° to 30°K., the amount of metal transforming in oxide-free, large-grained areas was of the order of 0·1%; this amount increased to about 1 to 10% on further cooling to 1·2°K. Barrett[15] has pointed out the important bearing of these findings on all past determinations of the physical properties of sodium at low temperatures. Specimens cast in small-diameter capillaries, where strain from differential contraction may be marked, will probably not show the same transformation temperatures as more massive samples. Specimens cast on copper wires or baffles might have intermediate transformation temperatures. Oxide films and oil films may also have an effect. If much plastic flow has occurred, a large hysteresis between cooling and heating experiments may be expected. In view of the unknown and varying amounts of transformation involved in previous determinations of electrical and thermal conductivity, thermoelectric effect, and specific heat, it is considered that they provide unreliable tests of physical theories of these properties in the low-temperature range.[15]

Preferential crystal orientation giving rise to a fibrous structure has been observed in threads of sodium after thermal and mechanical treatment, and the direction of the crystal orientation has been investigated.[8,16]

Glide occurs in single crystals of sodium when they are extended slightly.[4,17] The glide planes are visible as regular and parallel surface markings, and hardening occurs round them. With increase of temperature from -185° to 20°C. the glide plane changes successively from (112) to (110) to (123), but the direction of glide is in all cases [111].[17] At the lower temperatures the spacing of the glide planes is much closer than at room temperature. For a rate of flow of about 1% per minute, the critical shear stress is 7·1 g./mm.^{2} at -185°C., 5·3 at -82°C. and 4·9 at 20°C.[17]

A strong hysteresis has been found in the *X*-ray reflecting power of single sodium crystals when subjected to a cycle of heating and cooling, but this vanished when the crystals were chilled with liquid air.[18] The diffuse scattering of *X*-rays by sodium crystals has been the subject of both experimental and theoretical study.[19-23] Detailed evaluations of the surfaces of isodiffusion of sodium[19-21] are in close agreement with the experimental investigations of the diffuse scattering of *X*-rays by single crystals.[22,23]

The rate of crystallization of sodium on cooling the liquid below the melting point has been studied[24,25] and the effect of slight oxide contamination investigated.[24] Highly oxide-free sodium may be cooled 3·5° below the melting point before crystallization starts: for oxidized sodium the figure is never more than 2·5°.[24] In a study of the crystallization velocity of sodium agitated under xylene, it is reported that at temperatures below 98° dendritic crystals were obtained and at higher temperatures cylindrical crystals resulted.[25]

The structure of liquid sodium has been widely studied[26-30a] and several theoretical treatments and reviews have appeared.[31-38b] The liquid tends to retain a structure not dissimilar to that of the solid. Fig. 1 shows the radial distribution of atoms about any one atom in the liquid at 100°C. and at 400°C.:[29] the average density curves are included as dotted lines.

At the higher temperature the increased thermal agitation of the atoms has a smearing-out effect on the distribution curve. The first peak in the radial distribution curve occurs at about 3·83 A. for 100° and at about 3·90 A. for 400°C. These distances between atoms compare with a spacing of 3·7 A. in solid sodium at room temperature. In the solid, each atom has 8 nearest neighbours at this distance; zt greater distances there are then 6 further neighbours at 4·3 A., 12 at 6·1 A., 24 at 7·1 A. and 8 at 7·4 A. The second maximum in the radial distribution curve of the liquid is at about 7·0 A. for 100°C. and at 7·2 A. for 400°C. Earlier investigations gave values of 40·0 A.[28] (later corrected to 3·86 A.[29]) and 4·04 A.[26] for the first peak in sodium a little above its melting point. The radial distribution curves of Fig. 1 were obtained from the *X*-ray diffraction pattern by Fourier analysis utilizing the

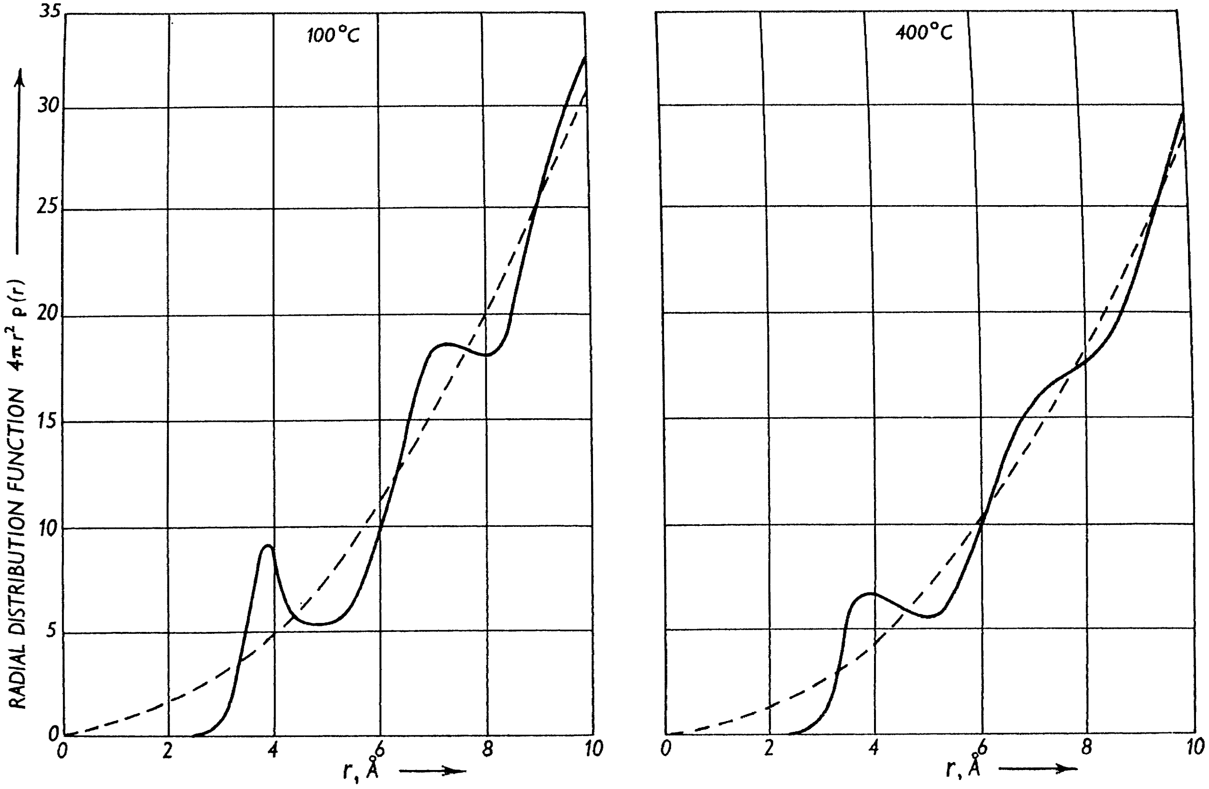

FIG. 1. RADIAL DENSITY DISTRIBUTION OF ATOMS ABOUT ANY ONE ATOM IN LIQUID SODIUM AT 100° AND 400°C.

Zernike and Prins[39] formula. Wall[34] developed a different distribution function for liquid sodium and fitted it to the same experimental data as used for Fig. 1. He found that at 100°C. each sodium atom has an average of 9·28 nearest neighbours at a distance of 3·79 A. corresponding to a free space of radius 0·6 A. At 400°C. there are 8·95 nearest neighbours lying at 3·80 A. and the free space radius is 0·77 A. On fusion there is thus an increase in the co-ordination number from its value of 8 in the solid. From the atomic distribution function, Wall has calculated the latent heats of fusion and vaporization of the metal with fair success.

Sodium provides a close approximation to the free electron model of the metallic state. This model, picturing a metal as a sea of free electrons in which are immersed a series of positive ions, has been used as a basis for theoretical calculations of many physical properties of sodium. In general, there is reasonably close agreement between the theoretical and experimental values.

Quantum mechanical treatments of the energy levels and of the bonding and cohesion in metallic sodium have been made by a number of authors.[40-60] In an early treatment, Slater[41] applied the London-Heitler method of homopolar binding to the calculation of the cohesive forces in sodium, but the approximation method developed by Wigner and Seitz,[43,44] and first applied to the case of sodium, has proved more successful in dealing with binding in the alkali metals. The Wigner-Seitz method uses the free electron picture and treats separately the valence electrons and the cores, it being assumed that the forms of the closed shells are not altered by metallic binding. If, in a monatomic body-centred cubic structure such as that of sodium, planes are drawn to bisect the lines joining an atom to each of its nearest and next nearest neighbours, the result is a set of space-filling 'atomic polyhedra' of 's-polyhedra', each taking the form of a truncated octahedron (Fig. 2). Since these have a fairly high symmetry, Wigner and Seitz make the approximation that they can be replaced by spheres of the same volume. A number of other simplifying assumptions are made concerning the occupation and interaction of these polyhedra, and wave functions are calculated for the valence electrons in their lowest state. The energy associated with the wave functions is used to obtain the cohesive or binding energy of the crystal.

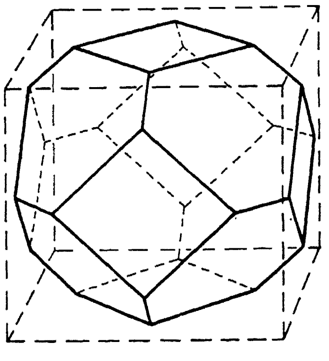

FIG. 2. ATOMIC POLYHEDRON SURROUNDING A SODIUM ATOM IN A BODY-CENTRED CUBIC STRUCTURE. THE CUBE DENOTES THE UNIT CELL.

A number of extensions and refinements[44-46,52-55,57] have been made to the original Wigner-Seitz method. Wigner[45] has included correlation forces, while Slater[46] and later workers[54,57] have extended the method to the computation of the excited bands of electrons in sodium. Kuhn and Van Vleck[55] have developed a method which, within the limits of spherical cell approximation, permits the evaluation of the cohesive energy and lattice constant of sodium without the computation of a central field for the atom. More recently Löwdin[55a] has calculated the cohesive energy using a linear combination of atomic orbitals and by introducing what he terms combined atomic orbitals. Although good agreement with experiment is obtained for the lattice parameter, reasons have been advanced for preferring the Wigner-Seitz approach.[57b] Values of the lattice constant and the cohesive or binding energy calculated by a number of authors are compared with the experimental values in Table I.

TABLE I.- CALCULATED AND EXPERIMENTAL VALUES FOR THE LATTICE CONSTANT AND COHESIVE ENERGY OF SODIUM

	Calculated							Experi-mental*
	Ref. (43)	Ref. (58)	Ref. (50)	Ref. (52)	Ref. (55)	Ref. (55a)	Ref. (57b)	
Lattice constant, A. units	4·2	4·51	4·35	4·53	4·14	4·26	4·27	4·23
Cohesive energy, kg.-cal./g.-atom	25·6	24·5	21·0	23	25·9	24·7	26·5	26

* The experimental values are extrapolated to 0°K.

In view of the approximate methods that have to be employed in the calculations, no great reliance can be placed on the exact numerical values. It is seen, however, that the theory of binding does give cohesive forces of the right order of magnitude. Since in the Wigner-Seitz method the assumption is made that the elementary cell can be replaced by a sphere, the energy becomes a function of atomic volume only and not of the crystal structure. It is not possible, therefore, in the present state of the theory to discuss allotropic transformations and to calculate, for example, the energy difference between the body-centred and face-centred forms of sodium.[60] More detailed reviews of the various quantum mechanical methods are available.[58-60]

Pauling[61] in formulating a set of ionic radii based on only five experimental interionic distances, namely those in NaF, KCl, RbBr, CsI and Li_2O, gave 0·95 A. for the radius of the Na^+ ion (Li^+, 0·60 A.; K^+, 1·33 A.; Rb^+, 1·48 A.; Cs^+, 1·69 A.). Goldschmidt[62] in an earlier treatment gave 0·98 A. for Na^+. These and other earlier treatments have been reviewed.[61,63]

Density and Thermal Expansion

The density of solid sodium has been reported as 0·9690 at 18°C.[64] and as 0·9735 at 20°C.[65] *X*-Ray measurements[7] lead to 0·9660 at 20°C. A figure of 0·9723 was previously given (Mellor, II, 452) as the best representative value at 20°C. In view of the variation among these figures there seems little justification at present in giving the density at room temperature to more than two significant figures. Low temperature measurements have given the density as $1{\cdot}01_5$ at 77°K. and $1{\cdot}01_0$ at 4·2°K.[66] At 100°K. the density calculated from *X*-ray data is 0·996: the value at 0°K. has been given as 1·01.[12]

Rinck[67,68] made measurements of the density of liquid sodium between approximately 400° and 600°C. which fitted the equation:-

$$d_4^t = 0{\cdot}9385 - 0{\cdot}000260(t - 96{\cdot}5).$$

This equation agrees closely with older density values at both the melting point[69] and the boiling point (Mellor, II, 453), and it was used by Rinck over the entire liquid range of sodium. More recent measurements[70] over the range 254° to 860°C. have led to the equation:-

$$d = (0{\cdot}9378 \pm 0{\cdot}0086) - (0{\cdot}000268 \pm 0{\cdot}000018)(t - 97{\cdot}5),$$

which is in close agreement with that of Rinck. Measurements by Novikov *et al.*[70a] from the melting point to 720°C. gave a good fit to a straight line, densities at 100°C. and 700°C. being 0·928 and 0·795 respectively. Other recent density values for liquid sodium are:-[71,72]

Temp., °C.	100	250	400	550	700
g./cm.^{3}	0·928	0·891	0·854	0·817	0·780

These data have been represented by the equations:-

$$d(\text{g./cm.}^3) = 0{\cdot}957 - 2{\cdot}7 \times 10^{-4}T \ (T \text{ in } ^\circ\text{C.})^{73}$$

$$\text{and } d(\text{lb./ft.}^3) = 63{\cdot}75 - 8{\cdot}766 \times 10^{-3}T + 9{\cdot}091 \times 10^{-8}T^{-2} \ (T \text{ in } ^\circ\text{F.}).^{74}$$

They give slightly lower densities than the first two equations quoted above. Density values at 5°F. intervals between 208°F. and 1500°F. have been listed[74] using the last equation. Rounded representative values for the density of sodium between 20° and 800° are given in Table II.

TABLE II.- DENSITY OF SODIUM

Temp., °C.	20	100	200	300	400	500	600	700	800
d	0·97	0·94	0·91	0·88	0·85	0·83	0·80	0·78	0·75

The increase in volume on fusion has been reported as 2·53%[65] and as 2·17%[64] or 0·0222 c.c. per gram.

The linear thermal expansion of single crystal specimens of sodium has been measured at 10° intervals between 80° and 290°K.[75] Some of the values are shown in Table III.

TABLE III.- THERMAL EXPANSION OF CRYSTALLINE SODIUM

T, °K.	$(l_T - l_{273}) \times 100/l_{273}$
80	−1·155
100	−1·071
120	−0·970
140	−0·860
160	−0·742
180	−0·621
200	−0·493
220	−0·361
240	−0·226
260	−0·090
280	+0·047
290	+0·116

Values for the mean coefficient of linear thermal expansion of sodium over the range 0 to 95°C. for pressures from zero up to 20,000 kg./cm.^{2} are given in Table IV.[76,77]

TABLE IV.- EFFECT OF PRESSURE ON THE THERMAL EXPANSION OF SODIUM

Pressure, kg./cm.^{2}	0	2000	4000	6000	8000	10,000
$\alpha(0 \text{ to } 95^\circ\text{C.}) \times 10^5$	7·1	$6{\cdot}2_2$	$5{\cdot}5_3$	$4{\cdot}9_5$	$4{\cdot}5_0$	$4{\cdot}0_8$

Refs. p. 411

TABLE IV continued

Pressure, kg./cm.^{2}	12,000	14,000	16,000	18,000	20,000
α(0 to 95°C.) × 10^5	$3{\cdot}7_0$	$3{\cdot}3_7$	$3{\cdot}3_0$	$2{\cdot}6_5$	$2{\cdot}3_3$

Fröhlich[51] has discussed the thermal expansion of sodium from a quantum mechanical standpoint. A later treatment by Balamuth[78] has given closer agreement with experiment.

Mechanical and Elastic Properties

Bridgman[76,77,79-85] has made extensive investigations of the effect of pressure on the volume of sodium. Table V, based on his more recent work, shows the relative volumes at room temperature for pressures up to 100,000 kg./cm.^{2}.[82,83]

TABLE V. - EFFECT OF PRESSURE ON THE VOLUME OF SODIUM AT ROOM TEMPERATURE

Pressure, kg./cm.^{2}	Relative Volume	Pressure, kg./cm.^{2}	Relative Volume
0	1·000	40,000	0·737
2,500	0·967	50,000	0·708
5,000	0·938	60,000	0·683
10,000	0·888	70,000	0·661
15,000	0·849	80,000	0·641
20,000	0·816	90,000	0·623
25,000	0·789	100,000	0·606
30,000	0·765		

The compressions of the five alkali metals are compared in Supplement 3. Equations[79] for the volume change at 30°C. and 75°C. with pressures up to 12,000kg./cm.^{2} require some revision in the light of later findings.[76,86] Another recent study[66] of the compression at low temperatures has given the figures in Table VI for the relative volumes of sodium at 4·2°K.

TABLE VI. - EFFECT OF PRESSURE ON THE VOLUME OF SODIUM AT 4·2°K.

Pressure, atmospheres	Relative Volume	Pressure, atmospheres	Relative Volume
0	1·000	3,000	0·962
500	0·993	4,000	0·951
1000	0·987	6,000	0·930
1500	0·980	8,000	0·912
2000	0·974	10,000	0·895

Bridgman[76] found that the compressibility of sodium increased with decrease of pressure to an extrapolated value of 17 × 10^{-12} cm.^{2}/dyne at zero pressure and room temperature. Earlier[79] he gave the initial compressibility at 30°C. as 15·62 × 10^{-12} cm.^{2}/dyne. Richards and co-workers[87] obtained a value of 15·6 × 10^{-12} cm.^{2}/dyne for the average compressibility of sodium at 25°C. for pressures between 10^8 and 5 × 10^8 dynes/cm.^{2} This is the same as the value given previously for 20°C. (Mellor,II,455). The same value has also been given for the compressibility at zero pressure and 80°K.[88] Other recent values[66] of the initial compressibility at low temperatures are 15·4 × 10^{-12} cm.^{2}/dyne at 77°K. and 13·7 × 10^{-12} cm.^{2}/dyne at 4·2°K. It should be pointed out that some earlier workers, including Richards, in giving pressures and compressibilities used the term 'megabar' to denote a pressure of 10^6 dynes/cm.^{2}: this usage is quoted in Mellor's original treatise. The term 'bar' is currently used to denote a pressure of 10^6 dynes/cm.^{2} To avoid any confusion, all values given in bars by the original authors have here been converted to dynes/cm.^{2}

Based on a value[89,89a] of 2526m./sec. for the velocity of ultrasonic waves in liquid sodium at its melting point (97·6°C.), the adiabatic compressibility has been found to vary from 16·85 × 10^{-12}cm.^{2}/dyne at the melting point to 19·02 × 10^{-12}cm.^{2}/dyne at 272°C.; the temperature coefficient changed only slightly from 0·012 × 10^{-12}cm.^{2}/dyne per degree C. at 97·6°C. to 0·013 × 10^{-12} at 272°C.[89a] Corresponding values for the isothermal compressibility are 19·11 × 10^{-12}cm.^{2}/dyne at the melting point and 22·19 × 10^{-12}cm.^{2}/dyne at 272°C.[89a] Another worker[90] gives 17·7 × 10^{-12}cm.^{2}/dyne for the adiabatic compressibility of liquid sodium at its melting point, and 21·0 × 10^{-12}cm.^{2}/dyne for the isothermal compressibility at the same temperature.

Theoretical treatments of the compressibility of sodium have been given by several authors.[43,50,51,53,55,91-94]

Using a test specimen of length 30 mm. and diameter 3 mm., the tensile strength of sodium at +17, −196 and −253°C. has been determined as 1·4, 1·9 and 4 kg./sq.mm. respectively.[95] The elongation at rupture for these three temperatures was 19, 18 and 60% respectively. Sodium thus becomes distinctly more plastic at low temperatures. For polycrystalline sodium rods,[96] the extension modulus at 20°C. is about 3 × 10^{10} dynes/cm., while the tension or rigidity modulus at this temperature is 9·6 × 10^9 dynes/cm. Measurements by Dawton[96] on single sodium crystals gave values varying between 31 × 10^9 and 14 × 10^9 for the extension modulus at 20°C., and between 9 × 10^9 and 35 × 10^9 for the torsion modulus, depending on the orientation of the crystal. Extrapolating to absolute zero from measurements in the range −183 to 90°C., Young's modulus was given as 56 × 10^9 dynes/cm. in the direction of the [100] axis: the torsion modulus was 15 × 10^9 dynes/cm. in the [110] direction and 59 × 10^9 dynes/cm. in the [100] direction.[96]

For cubic crystals such as sodium there are only three independent values for the elastic 'moduli' or compliances (S_{11}, S_{12} and S_{44}), and for the elastic constants (C_{11}, C_{12} and C_{44}). Values of the adiabatic elastic constants between 80° and 210°K. are given in Table VII.[5] Isothermal constants derived from them are given in Table VIII. The isothermal values of S_{44} and C_{44} are the same as the respective adiabatic values. The estimated uncertainty in the absolute values in Tables VII and VIII is 2–3%.

TABLE VII. - ADIABATIC ELASTIC CONSTANTS OF SODIUM

T°K.	cm.^{2}/dyne × 10^{-11}			dynes/cm.^{2} × 10^{11}		
	S_{11}	$-S_{12}$	S_{44}	C_{11}	C_{12}	C_{44}
80	4·826	2·087	1·685	0·608	0·463	0·593
100	4·898	2·118	1·726	0·598	0·456	0·579
120	4·975	2·151	1·770	0·589	0·448	0·565
140	5·054	2·186	1·818	0·581	0·443	0·550
160	5·135	2·224	1·874	0·576	0·440	0·534
180	5·220	2·262	1·936	0·568	0·434	0·516
200	5·308	2·301	2·002	0·560	0·428	0·499
210	5·354	2·321	2·037	0·555	0·425	0·491

Elastic constants obtained by Bender[6] at −183°C. (C_{11} = 0·945 × 10^{11} dynes/cm.^{2}, C_{12} = 0·779 × 10^{11} dynes/cm.^{2} and C_{44} = 0·618 × 10^{11} dynes/cm.^{2}) are considerably higher than those in the above Tables Values at absolute zero

TABLE VIII. - ISOTHERMAL ELASTIC CONSTANTS OF SODIUM

T°K.	cm.^{2}/dyne × 10^{-11}		dynes/cm.^{2} × 10^{11}	
	S_{11}	$-S_{12}$	C_{11}	C_{12}
80	4·829	2·084	0·601	0·456
100	4·901	2·115	0·592	0·449
120	4·977	2·147	0·581	0·441
140	5·058	2·181	0·571	0·432
160	5·140	2·218	0·564	0·428
180	5·226	2·256	0·556	0·422
200	5·315	2·294	0·546	0·415
210	5·361	2·313	0·541	0·410

from the quantum mechanical calculations of Fuchs[97,98] are $C_{11} = 0{\cdot}97 \times 10^{11}$ dynes/cm.^{2}, $C_{12} = 0{\cdot}83 \times 10^{11}$ dynes/cm.^{2} and $C_{44} = 0{\cdot}58 \times 10^{11}$ dynes/cm.[22] Other values of the elastic constants have been calculated by Bulashevich[99] and by Totani.[99a]

The relation between the diffuse reflection of X-rays by a set of planes in a crystal and the normal (Bragg) reflection is determined by the elastic constants of the crystal. This has been studied and discussed for the case of sodium.[19-23]

Sodium shows an unusually great increase in its shearing strength with increase of pressure, and with decreasing pressure there is an unusually large hysteresis.[100] At a hydrostatic pressure of 50,000 kg./cm.^{2} the shearing stress for plastic flow is 5200 kg./cm.^{2}.[100]

No recent work appears to have been done on the hardness of sodium.

Surface Properties

Determinations of the surface tension of sodium have been carried out by a number of methods, the majority of them leading to a value of about 200 dynes cm.$^{-1}$ for the surface tension at the melting point. Measurements on a sessile drop of sodium in a vacuum gave 206·4 dynes cm.$^{-1}$ at 100°C. and 199·5 dynes cm.$^{-1}$ at 250°C., the temperature coefficient being -0·046 dynes cm.$^{-1}$ degree^{-1}.[101] Capillary-rise in glass has given 110 to 125 dynes cm.$^{-1}$ in the lower temperature range,[72] while the maximum bubble pressure method has given 190·8 dynes cm.$^{-1}$ at the melting point with a temperature coefficient of -0·1 dynes cm.$^{-1}$ degree^{-1} from the melting point up to 450°C.[102-104] By the use of a vertical plate technique,[73] γ = 186 dynes cm.$^{-1}$ was found at 180°C.; the temperature coefficient was -0·1 dynes cm.$^{-1}$ degree^{-1} which by extrapolation gives γ = 195 dynes cm.$^{-1}$ at the melting point of sodium. Measurements by a drop-volume method[105] over the temperature range 110-220° have also given a temperature coefficient of -0·1 dynes cm.$^{-1}$ degree^{-1}, and extrapolation to the melting point gave γ = 202 dynes cm.$^{-1}$ A theoretical treatment[106] has given -0·09 dynes cm.$^{-1}$ degree^{-1} for the temperature coefficient of the surface tension.

Calculations[107-114] of the surface energy of sodium using electronic theories have given values both considerably greater and considerably smaller than those obtained experimentally. Thus, values calculated by the use of the free-electron model have ranged from about one quarter[111] to three times[109] the mean observed value. The value in closest agreement with experiment is γ = 190 dynes cm.$^{-1}$ calculated by Stratton.[113]

A film of sodium oxide on the surface of sodium metal increases the apparent surface tension,[73,102,103,115] but if oxide is present below its solubility limit it may have the opposite effect.[73,115] The interfacial tension between liquid sodium and sodium crystals has been given as 2dynes cm.$^{-1}$ for samples very free from oxide;[24] slight oxide contamination can reduce the figure by a factor of four.

From the surface tension of metallic sodium the parachor is 92. Values of the parachor calculated from surface tension data for fused salts[116] and for salts in solution[117] are 80 and 90 respectively.

Numerous metals are said to show a critical temperature of wetting by sodium.[73,118] Above this critical temperature, wetting by sodium is a ready process; below it, wetting occurs with difficulty if at all. The wetting temperature of zinc lies between 128° and 180°, and it has been reported that copper and molybdenum are not wetted at these temperatures.[73] Miller *et al.*[119] determined the wetting temperature of nickel as 355 ± 5°C., and that of low-carbon steel as 370 ± 5°C. Other workers,[118,120] however, have reported that clean surfaces of molybdenum and low-carbon steel are wetted by sodium at its melting point, and that the wetting temperatures for clean surfaces of nickel, stainless steel 347 (18% Cr, 10% Ni, 1% Nb), and glass are 230-260°, 138-168°, 306-333°C. respectively. Coatings of oxide or grease have a considerable effect on the wetting temperature,[118,120] and such coatings are, no doubt, responsible for the variable results that have been recorded. In the last mentioned investigations, the wetting temperatures of oxide-coated molybdenum and low-carbon steel, for example, were raised to 267° and 292-426°C. respectively.[118,120] Sodium oxides are not wetted by liquid sodium.[73] The wetting of metals by sodium-potassium alloys has also been studied.[121]

High Surface Sodium, Sodium Dispersions and Colloidal Sodium

Liquid sodium spreads over many inert substances of large surface area, e.g., salt, carbon, alumina and metal powders, to give a covering film which may approach atomic dimensions in thickness.[122] Quite high percentages of sodium may be adsorbed in this way without the solids losing their free flowing characteristics. Sodium chloride, depending on its crystal size, will carry 2-10% of sodium; sodium carbonate will carry 10% of sodium; alumina, 20-25% of sodium; and activated or colloidal carbons, over 30% of sodium. At higher sodium concentrations the mixtures become pasty. Provided that the carrier is temperature-stable, the free flowing characteristics can be maintained up to the boiling point of sodium. Certain substances such as aniline, colloidal carbon and colloidal metals are reported to facilitate the spreading of sodium over inert materials. A number of high-surface sodium systems are described in Table IX.[122]

Dispersions of sodium may be produced in many inert liquids such as toluene, xylene, heptane and *n*-butyl ether, which have boiling points above the melting point of sodium, by heating the mixture of sodium and inert liquid to between 100 and 110°C. and then applying vigorous mechanical agitation. Several laboratory and plant scale dispersion units have been described.[123] Sodium particles with diameters ranging from 20 microns to less than one micron may be obtained depending on the method of preparation, and the dispersions may contain up to 50% of sodium. In general, the dispersions have nearly the same fluidity as the dispersing medium, and properly formulated dispersions may be used above or below the melting point of sodium without coalescence of the particles. Certain additives assist in the preparation of sodium dispersions. Some metal powders, for example, serve to break down the sodium particle size but do not stabilize the dispersions. Other materials - such as the aluminium salts of long chain fatty acids - as well as assisting in particle size breakdown, give dispersions which do not ordinarily coalesce in three months.[123] The patent literature contains numerous references to other dispersing and stabilizing agents for use in the preparation of

TABLE IX. - HIGH SURFACE SODIUM SYSTEMS

Solid Carrier	Optimum Dispersing Temp., °C.	% Sodium	Appearance
Sodium Chloride 130–420 μ	150	2–10	Grey to black salt
Sodium Carbonate 50–150 μ	150	10	Grey to black powder
Activated Alumina	140–160	20–25	Black or mottled white granules
Activated Carbon (coconut)	120	35+	Silver to black pyrophoric powder
Colloidal Carbon	170	>30	Black pyrophoric powder
Iron Powder 150 μ	150–200	5	Grey powder
White Sand 420–840 μ	150–165	5	Grey surfaced sand
Zirconium Oxide <50 μ	250	10	Dark grey powder

sodium dispersions.

Colloidal solutions of sodium have been prepared by condensation methods.[124-127] Sodium vapour may be passed into the cooled dispersion liquid, or the mixed vapours of sodium and the dispersion medium may be condensed on a cooled surface. Reduced pressures are usually used in both cases. Tomashevskii,[125] using such methods, prepared sodium sols in ether which were stable for a month; they showed an absorption spectrum from 6238 to 4696 A. with the violet end polarized. Sodium sols in xylene were stable for twelve to twenty hours, while sols in benzene had a dirty-green colour and were stable for three days. Lauer[128] prepared ~0·3% sodium sols in ether by passing an alternating or direct current between a dipping electrode and sodium spheres under the ether. Ultrasonic waves have also been used in preparing colloidal solutions of sodium.[129,130b]

Sodium dispersions and other high-surface forms of sodium find many applications in chemical reactions (see pages 427–547).

Viscosity

Viscosity measurements for sodium, made up to 200°C.[131] using a glass Ostwald-type viscometer and at higher temperatures up to 700°C.[132] using a similar apparatus in nickel, are given in Table X. The values up to 200°C. have been represented by the equation:-

$$\eta v^{1/3} = 1{\cdot}089 \times 10^{-3} e^{756{\cdot}9/vT},$$

and those for the whole range from the melting point to 700°C. by:-

$$\eta v^{1/3} = 1{\cdot}142 \times 10^{-3} e^{739{\cdot}8/vT}$$

where v is the specific volume and T the absolute temperature. These measurements are in close agreement with others[133] carried out by an oscillating

TABLE X.- VISCOSITY OF SODIUM

Temp., °C.	Viscosity, c.g.s. units × 10^2	Temp., °C.	Viscosity, c.g.s. units × 10^2
103·7	0·686	292	0·354
121·6	0·620	371	0·308
147·0	0·548	447	0·270
167·0	0·504	506	0·240
192·7	0·460	571	0·216
250	0·388	686	0·183

sphere method from the melting point to 355°C. ($\eta = 0{\cdot}7264 \times 10^{-2}$ c.g.s. at 98°C., $0{\cdot}3015 \times 10^{-2}$ c.g.s. at 355°C.), the maximum disagreement being less than 2% at 350°C. The last mentioned results were expressed by the equation:-

$$\eta v^{1/3} = 1{\cdot}142 \times 10^{-3} e^{600{\cdot}0/vT}$$

except near the melting point where higher viscosities were obtained suggesting the persistence of a crystal structure for a few degrees above the melting point. Damping characteristics of torsional oscillations in a freely suspended crucible containing sodium were also studied by Novikov *et al.*[70a] to obtain the kinematic viscosity ($\nu = \mu$/density) between the melting point and 800°C. Interpolated values of kinematic viscosity from the graphically presented results are:-

Temp.°C.	100	150	200	300	400	500	600	700	800
ν (c.g.s. units × 10^2)	0·80	0·58	0·50	0·39	0·33	0·29	0·26	0·23	0·21
η (c.g.s. units × 10^2)	0·74	0·53	0·45	0·35	0·28	0·24	0·21	0·18	0·16

The last line shows viscosities obtained by combining the kinematic viscosities with the same workers' density determinations. There is close agreement with the previous measurements.[132,133] Other earlier and less precise measurements made in the vicinity of the melting point gave values several per cent. higher than those quoted above.[134,135] Experimental values for the viscosity of sodium have been related to the binding energy of the molecules of the liquid and to the entropy of bond formation.[136]

Diffusion

The coefficient of self-diffusion for solid sodium increases from $9{\cdot}22 \times 10^{-10} \pm 2{\cdot}47 \times 10^{-10}$ cm.²/sec. at 0°C. to $1{\cdot}43 \times 10^{-7} \pm 0{\cdot}02 \times 10^{-7}$ cm.²/sec. at 95°C., and at one atmosphere pressure the temperature variation may be expressed by the equation:-[1]

$$D_{\text{solid}}\ (\text{cm.}^2/\text{sec.}) = 0{\cdot}242e^{-10{,}450/RT}$$

Hydrostatic pressure decreases the rate of self-diffusion; at 8000 atmospheres the equation becomes:-[137]

$$D_{(8000\ \text{atm.})}\ (\text{cm.}^2/\text{sec.}) = 0{\cdot}176e^{-12{,}060/RT}.$$

When both are considered as a function of pressure, the free energy of activation is a linear function of the melting point.[137] Similarly the enthalpy of activation is related to the latent heat of fusion by the equation, $H = 16{\cdot}5\ L_m$. There is an increase in the rate of self-diffusion at the melting point; at one atmosphere pressure, $D_{\text{solid}} = 2{\cdot}16 \times 10^{-7}$ cm.²/sec. at 97·83°C. and $D_{\text{liquid}} = 4{\cdot}19 \times 10^{-5}$ cm.²/sec. at 98·0°C.[138] The diffusion coefficient for the liquid between the melting point and 226°C. may be represented by the equation:-[139]

$$D_{\text{liq.}}\ (\text{cm.}^2/\text{sec.}) = 1{\cdot}10 \times 10^{-3}e^{-2430/RT}$$

Self-diffusion in sodium has been discussed in relation to its nuclear magnetic resonance,[140,141b] and from nuclear resonance data the coefficient of self-diffusion at −56°C. has been estimated[141] as 1·3 × 10^{-11} The activation energy of self-diffusion has been estimated as 9·5 ± 1·5 kg.-cal./g.atom from nuclear magnetic resonance data[140] and as 9·1 ± 0·1 kg.-cal./g.atom from the anomalous rise of electrical resistance that starts well below the melting point.[141c,d] The mechanism of self-diffusion in alkali metals has been discussed by Paneth.[142]

Diffusion of sodium vapour in nitrogen and other gases has been studied in connexion with the use of sodium in diffusion flame experiments.[143,144] Measurements were actually made at pressures of about 1 to 4 mm. of mercury, but it is usual to assume that the diffusion constant is inversely proportional to the total pressure and to give the results for a total pressure of one atmosphere. In nitrogen at one atmosphere the diffusion constant is 0·68 ± 0·03 cm.^{2}/sec. at 253·5°C.[144] and 0·91 cm.^{2}/sec. at 382°C.[143] Other diffusion constants at approximately 380°C. and one atmosphere pressure are 3·14 cm.^{2}/sec. in hydrogen, 2·17 cm.^{2}/sec. in helium, 0·88 cm.^{2}/sec. in argon and 0·23 cm.^{2}/sec. in pentane vapour.[143] Measurements have also been made in hydrogen-nitrogen, hydrogen-argon, hydrogen-pentane and nitrogen-pentane mixtures.[143] At 15°C. and a pressure of 1 mm. mercury the diffusion constant of sodium in nitrogen has been given as 20·4 cm.^{2}/sec.[145] Other measurements have been made of the diffusion of sodium atoms in flames at temperatures of about 1700-2100°K.[146,147]

When alkali halide crystals are heated in an alkali metal vapour, or when crystals with alkali metal imbedded in the side are heated to 400-800°C., the crystals assume a deep colour and acquire a stoicheiometric excess of alkali metal. The colour of these 'Farbzentren' is characteristic of the crystal and not of the alkali metal. Diffusion of sodium atoms into sodium chloride crystals under such conditions has been studied.[148-150] With the aid of the ultramicroscope it has been shown that the diffusion follows cracks in the crystal lattice.[150]

Ransley and Neufeld[151] have studied the diffusion of sodium in aluminium: approximate values for the diffusion coefficient are 2 × 10^{-9} cm.^{2}/sec. at 550°C., 1 × 10^{-8} cm.^{2}/sec. at 600°C., and 7 × 10^{-8} cm.^{2}/sec. at 650°C. The coefficient of diffusion of sodium in mercury at 8 to 15°C., as calculated from atomic radius and viscosity data with the aid of the Stokes-Einstein equation, is 0·59 cm.^{2} per 24 hours.[152] This figure is in reasonable agreement with the older experimental value of 0·64 cm.^{2} per 24 hours (Mellor, II, 456). Measurements of the diffusion of sodium in mercury at 22°C. have given D = 0·80 × 10^{-5} ± 0·04 × 10^{-5} cm.^{2}/sec.(≡ 0·69 cm.^{2} per 24 hours)[152a]

Melting Point and Heat of Fusion

The triple point of pure sodium is 97·82 ± 0·02°C.[153,153a] An earlier measurement by the same workers gave 97·80 ± 0·03°C., and the melting point of the pure metal at a pressure of one atmosphere was calculated to be 0·01°C. higher than the triple point.[154] Other measurements of the melting point have given values only slightly different from this, viz. 97·91 ± 0·06,[138] 97·8 ± 0·1,[155] 97·7 ± 0·1,[64] 97·7[156] and 97·6°C.[157] The melting point increases with increase of pressure, and a value of 350°C. has been estimated for the limiting melting point at high pressures.[158] Melting point-pressure curves for the alkali metals are compared in Supplement 3, the sodium curve being based on previously quoted determinations (Mellor, II, 456).

A recent calorimetric determination has given 113·2 ± 0·4 joule/g. (equivalent to 27·05 g.-cal./g.) for the latent heat of fusion of sodium.[154] This agrees well with the values of 27·1 and 27·2 g.-cal./g. reported previously (Mellor,II,457). Kelley[159] has discussed the calculation of the heat of fusion of sodium from freezing point data for binary sodium systems. A rounded average value of 640 g.-cal./g.atom (≡ 27·8 g.-cal./g.) was obtained using the results of several workers for the systems Na-Au, Na-Hg and Na-Tl. A number of other binary systems, including Na-Al, Na-Ag, Na-Bi, Na-Ca Na-Li, Na-Mg, Na-Pb, Na-Sb, Na-Sn and Na-Zn, are considered to be unsuitable for calculating the heat of fusion of sodium owing to the existence of either a eutectic or two liquid phases near 100% sodium.

Theoretical calculations of the heat of fusion of sodium have appeared,[34,35] and relationships between the heat of fusion, the variation of melting point with pressure, and the volume change on fusion have been discussed.[158,160-162a] A value of 27·3 g.-cal./g. was obtained for the heat of fusion from a relationship between the parachor and the heat of fusion.[163]

Vapour Pressure, Boiling Point and Degree of Association

A number of independent measurements of the vapour pressure of sodium have been made at temperatures below its boiling point. These have led to the following equations, all of which give closely concordant values; p is in mm. of mercury and T in °K.

Temperature Range °C.	Vapour Pressure Equation	Reference
473–565	$\log_{10} p = -5780/T + 11{\cdot}435 - 1{\cdot}178 \log T$	164
182–597	$\log_{10} p = -5922/T + 12{\cdot}9605 - 1{\cdot}6184 \log T$	165
220–300	$\log_{10} p = -5573{\cdot}3/T + 9{\cdot}7255 - 0{\cdot}6794 \log T$	156
341–498	$\log_{10} p = -5773/T + 12{\cdot}439 - 1{\cdot}52 \log T$	155
341–498	$\log_{10} p = -5720/T + 11{\cdot}396 - 1{\cdot}178 \log T$	166, 155
665–768	$\log_{10} p = -5400/T + 7{\cdot}5510$	167
263–396·5	$\log_{10} p = -5400/T + 7{\cdot}551$	168

Measurements of the magnetic rotation of the plane of polarization of light by sodium vapour between 509° and 695°K.[169] have led to the equation $\log_{10} p$ (mm.) $= -5690/T + 11{\cdot}333 - 1{\cdot}178 \log T$ for the vapour pressure.[170] Using specific heat data together with the vapour pressure of sodium at one temperature, Millar[171] represented the vapour pressure of liquid sodium by the equation: $\log_{10} p$ (mm.) $= -5135/T + 11{\cdot}071 - 1{\cdot}20 \log T$; and that for solid sodium by:-

$$\log_{10} p \text{ (mm.)} = -7091{\cdot}9/T - 4{\cdot}6050 + 15{\cdot}0560 \log T - 2{\cdot}7136 (\log T)^2.$$

Rowe[172] in 1927 reviewed early work on the vapour pressure of sodium; he gave 4×10^{-13} mm. as the most probable vapour pressure of sodium at 0°C. In the same year, Rodebush[173] fitted the results of several investigators[156,164,165] to the equation $\log_{10} p$ (mm.) $= -5730/T + 11{\cdot}580 - 1{\cdot}25 \log T$. Numerous values for the vapour pressure of sodium reported prior to 1930–32 have been summarized and reviewed by Ladenburg and Thiele.[155,166] On the basis of data available up to 1934, Kelley[174] represented the total vapour pressure of liquid sodium by the equation:-

$$\log_{10} P\text{(atm.)} = -5775/T + 8{\cdot}863 - 1{\cdot}274 \log T.$$

From a graphical analysis of all the above data, Ditchburn and Gilmour[175] in 1941 gave the equation:-

$$\log_{10} p \text{ (mm.)} = -5562/T + 9{\cdot}235 - 0{\cdot}5 \log T$$

as representing the vapour pressure of sodium within ± 5% between 450° and 1200°K. and within ± 10% between 370° and 1250°K.

Recent measurements[176,177] have extended vapour pressure values up to several atmospheres. For these the boiling point of triply-distilled sodium was determined under various argon pressures, and the results over the pressure range 0·047 to 6·489 atmospheres were fitted by the equation:-[177]

$$\log P(\text{atm.}) = -5220/T + 4{\cdot}521$$

with a standard error in P of 0·9%. Temperatures at which the vapour pressure assumes rounded values calculated from this last equation and from the equation of Ditchburn and Gilmour[175] are given in Table XI.

TABLE XI. - VAPOUR PRESSURE OF SODIUM

Pressure, mm.Hg.	10^{-3}	10^{-2}	10^{-1}	1	10	10^2	760	10^3	10^4
T, °K. (Ref. 175)	511	564	630	713	821	969	1154	1180	1525
T, °K. (Ref. 177)	502	555	621	705	815	966	1154	1186	1534

The two sets of values agree within the error limit of the former equation over the range 100 to 1000 mm.; elsewhere the deviation exceeds this error limit. According to the latest investigators,[177] none of the presently available equations for sodium can be used safely to predict vapour pressure values above 5000 mm.Hg.

The recent measurements on triply-distilled sodium referred to above give the boiling point at one atmosphere as 881·3°C.[177] Extrapolation of vapour pressure data obtained at lower temperatures leads to values for the boiling point in close agreement with this. Thus, as seen from Table XI, the vapour pressure equation of Ditchburn and Gilmour,[175] which was obtained by graphical analysis of all previous vapour pressure measurements, gives a value of 881°C. for the boiling point.

At low pressures sodium vapour is largely monatomic, but with increase of pressure the percentage of molecules increases until at one atmosphere - *i.e.* at the normal boiling point - sodium molecules are present to the extent of about 15% by volume.

Values of the equilibrium constant for the dissociation of diatomic sodium vapour into atoms, computed by Gordon[178] from spectroscopic data, are given in Table XII (partial pressures in atmospheres).

Combining these figures with the vapour pressure data of several investigators, Gordon gave the following equation for the vapour pressure of monatomic sodium vapour:-

$$\log_{10} p_{\text{Na}}\ (\text{mm.}) = -5702/T + 11{\cdot}3245 - 1{\cdot}174 \log T.$$

TABLE XII. - DISSOCIATION CONSTANT FOR DIATOMIC SODIUM VAPOUR

T, °K.	298·1	400	600	800	1000
Log Kp = log $(P_{\text{Na}})^2/P_{\text{Na}_2}$	-9·165	-5·797	-3·816	-0·823	+0·184
T, °K.	1200	1400	1600	1800	2000
Log Kp = log $(P_{\text{Na}})^2/P_{\text{Na}_2}$	0·857	1·339	1·702	1·981	2·204

The partial pressures of atoms and molecules in the saturated vapour at the boiling point predicted by this equation (1162°K.) are 658 mm. and 102 mm. respectively. More recent calculations of the dissociation constant, also using spectroscopic data, have been carried out by Benton and Inatomi.[179] Their values for log Kp include -8·66 at 298·1°K., 0·34 at 1000°K., 2·31 at 2000°K. and 2·77 at 2600°K. (partial pressures in atmospheres). Values for the molecular weight of sodium vapour between 100° and 2600°K. (at a total pressure of one atmosphere) based on these last results are included in Table XVI (see page 397). Ladenberg and Thiele[155] calculated dissociation constants and combined them with other vapour pressure data to obtain the equation:-

$$\log_{10} p_{\mathrm{Na}}(\mathrm{mm.}) = -5701/T + 11{\cdot}329 - 1{\cdot}178 \log T.$$

At the boiling point (1156°K.) this gives $p_{\mathrm{Na}} = 614$ mm. and $p_{\mathrm{Na}_2} = 145$ mm. Lewis,[180] using a magnetic deflection method, obtained experimental values for the dissociation constant ranging from log Kp (partial pressures in mm.Hg) = 0·936 at 630°K. to log Kp = 2·06 at 762·5°K. (equivalent to −1·945 to −0·82 for partial pressures in atmospheres). From calculations based on the results of Lewis, the partial pressures of sodium atoms and molecules have been expressed by the equations:-[175]

$$\log_{10} p_{\mathrm{Na}} = -5728/T + 11{\cdot}641 - 1{\cdot}27 \log T$$
$$\log_{10} p_{\mathrm{Na}_2} = -7020/T + 8{\cdot}149.$$

The accuracy of the former equation is stated to be ± 10% between 370° and 850°K., and ± 20% between 370° and 1200°K.; that for the latter is ± 50% between 600° and 800°K.

Determinations of the vapour density of sodium made between 570° and 706°C. using a dynamic method have given values for the apparent molecular weight which are lower than those predicted by spectroscopic data.[167,181]

From the slope of his log Kp − $(1/T)$ curve, Lewis[180] calculated a value of 16·5 kg.-cal./g.mole (≡ 0·73 e.V.) for the heat of dissociation or dissociation energy of the sodium molecule. From the magnetic rotation spectrum, Loomis and Nusbaum[182] obtained a value of 0·76 ±0·02 e.V. An earlier determination[183] of the heat of dissociation from band spectra data gave a much higher value of 26·8 kg.-cal./g.mole (≡ 1·16 e.V.). Rodebush[184] in 1932 considered that the true value was in the interval 0·76–0·78 e.V. Herzberg in 1950[185] listed 0·73 e.V. as the best value of the dissociation energy. The U.S. Bureau of Standards selected value[187] for the heat of formation of diatomic sodium vapour is 34·58 kg.-cal./g.mole at 0°K. and 33·97 kg.-cal./g.mole at 298·16°K., while the free energy of formation at the latter temperature is 24·85 kg.-cal./g.mole. A later publication[187a] gives the heat of formation of diatomic vapour as 34·31 kg.-cal./g.mole at 0°K. and 33·705 kg.-cal./g.mole at 298·16°K.; the free energy of formation at 298·16°K. is given as 24·637 kg.-cal./g.mole.

Heats of Vaporization and Sublimation

Values for the heat of vaporization of sodium at 0°K., calculated from vapour pressure data, include 25·8 kg.-cal./g.-atom,[186] 25·9 kg.-cal./g.-atom,[170] 26·0 ± 0·13 kg.-cal./g.-atom,[155] and 26·2 ± 0·13 kg.-cal./g.-atom.[166] Between 540° and 840°K., Ladenberg and Minkowski[170] gave the equation ΔH(kg.-cal./g.-atom) = $25{\cdot}95 - 2{\cdot}34 \times 10^{-3}T$, while Rodebush and De Vries[165] gave the heat of vaporization near the melting point as 24·6 kg.-cal. Using the composite data of several workers, Kelley[174] has represented the heat of vaporization to monatomic vapour by the equation:-

$$\Delta H(\mathrm{kg.\text{-}cal./g.\text{-}atom}) = 26{\cdot}124 - 2{\cdot}53 \times 10^{-3}T,$$

and the free energy of vaporization by:-

$$\Delta F(\mathrm{kg.\text{-}cal./g.\text{-}atom}) = 26{\cdot}124 + 5{\cdot}83 \times 10^{-3}T \log T - 3{\cdot}993 \times 10^{-2}T.$$

For the temperature at which the pressure of atoms becomes one atmosphere (1187°K.), ΔH is 23·121 kg.-cal./g.-atom and ΔS is 19·48 g.-cal./g.-atom.[174]

The U.S. Bureau of Standards[187] selected value for the heat of sublimation of sodium to monatomic vapour is 26·05 kg.-cal./g.-atom at 0°K. and 25·98 kg.-cal./g.-atom at 298·16°K., while the value for the free energy of sublimation is 18·67kg.-cal./g.atom at 298·16°K. A later publication[187a] gives the heat of sublimation to monatomic vapour as 25·92kg.-cal./g.atom at 0°K. and 25·857kg.-cal./g.atom at 298·16°K., and the free energy of sublimation as 18·574kg.-cal./g.atom at 298·16°K. Kelley[174] has given the equations:-

$$\Delta H(\text{kg.-cal./g.-atom}) = 26\cdot199 - 0\cdot4 \times 10^{-4}T - 2\cdot68 \times 10^{-6}T^2$$

$$\text{and } \Delta F(\text{kg.-cal./g.-atom}) = 26\cdot199 - 0\cdot9 \times 10^{-4}T \log T + 2\cdot68 \times 10^{-6}T^2 - 2\cdot638 \times 10^{-2}T$$

for the heat and free energy of sublimation respectively. These lead to $\Delta H_{298\cdot1}$ = 25·949 kg.-cal./g.-atom and $\Delta F_{298\cdot1}$ = 18·639 kg.-cal./g.-atom. Quantum mechanical computations of the heat of sublimation or cohesive energy of sodium have been made by a number of authors[43,44,50-53,55-55b] (see page 381).

Specific Heat, Enthalpy and Entropy

Specific Heat.

The specific heat of sodium at low temperatures has been studied by several investigators. Simon and Zeidler[188] in 1926 made measurements above 17°K.:-

T, °K.	16·95	20·04	23·35	26·17	29·4
C_p, g.-cal./g.-atom/°C.	0·592	0·856	1·21	1·55	1·93
C_v, g.-cal./g.-atom/°C.					
T, °K.	34·6	41·4	49·5	58·1	117·6
C_p, g.-cal./g.-atom/°C.	2·47	3·09	3·79	4·27	5·64
C_v, g.-cal./g.-atom/°C.		3·09	3·78	4·24	5·50

More recently (1950), Pickard and Simon[189] made measurements between 2° and 25°K. In the overlapping temperature range the values were slightly higher than those obtained previously.

T, °K.	2	4	6	7	8	10
C_v, g.-cal./g.-atom/°C.	0·0055	0·0135	0·059	0·124	0·093	0·140
T, °K.	12	14	16	18	20	25
C_v, g.-cal./g.-atom/°C.	0·250	0·385	0·54	0·71	0·90	1·45

There is an anomalous behaviour at about 7°K. where a peak occurs in the specific heat–temperature curve. A study of the specific heat at temperatures below 1°K. has also shown a pronounced peak at about 0·87°K.[190] A low-temperature martensitic-type transformation (see page 377) has been suggested as the cause of this behaviour. Parkinson and Quarrington,[191] employing sodium specimens that had been allowed to self-anneal for several days, observed no peak in the range 1·4 to 20°K., and they suggest that in the above two instances where anomalies have been observed the specimen was probably in a state of strain. The specific heat values obtained in this last study were:-

T, °K.	1·5	2·0	3·0	4·0	5·0
C_p, g.-cal./g.-atom/deg.	0·00105	0·00180	0·00445	0·00985	0·0195
T, °K.	6·0	7·0	8·0	10·0	12·0
C_p, g.-cal./g.-atom/deg.	0·0345	0·052	0·078	0·142	0·250

T, °K.	14·0	16·0	18·0	20·0
C_p, g.-cal./g.-atom/deg.	0·385	0·535	0·710	0·900

They agree well with those of Pickard and Simon between 10° and 20°K., but at lower temperatures they are considerably below the earlier values. Measurements by Roberts[191a] over the range 1·3 to 20°K. have also shown a monotonic increase of specific heat with temperature, but the values recorded were between 5 and 10% lower than those of Parkinson and Quarrington.[191] Plots of C_p/T against T^2 for the results of Parkinson and Quarrington[191] and of Roberts[191a] lead to values of $0{\cdot}00043\,T$ g.-cal./g.atom^{-1}deg.$^{-1}$ and $(0{\cdot}000328 \pm 0{\cdot}00001)T$ g.-cal./g.atom^{-1}deg.$^{-1}$ respectively for the electronic specific heat. Bidwell[192] calculated the specific heat of sodium at temperatures between that of liquid hydrogen and 70°C. using cooling curves obtained in a study of the thermal conductivity of sodium. At temperatures above −125°C. the atomic heat at constant volume exceeded the Dulong and Petit maximum, and it was suggested that the excess represented latent heat of crystallization required for disintegration of the crystal lattice. In other measurements extending from 55° to 315°K. it was found that in the region between 150° and 250°K. the specific heat curve showed a very slight hump which rose to a peak of approximately ½% above the smooth line joining the upper and lower parts of the curve.[192a] A hysteresis effect was also found in this region.[192a] Table XIII[189] gives values for the specific heat of sodium up to 300°K. based on the measurements of several workers.

TABLE XIII. - THERMODYNAMIC PROPERTIES OF SODIUM AT LOW TEMPERATURES

Temp. °K.	C_p g.-cal./g.-atom/°C.	$H_T{-}H_0$ g.-cal./g.-atom	$S_T{-}S_0$ g.-cal./g.-atom/°C.	$-(F_T{-}F_0)$ g.-cal./g.-atom
0	0·0	0·0	0·0	0·0
10	0·135	0·452	0·067	0·118
20	0·905	5·23	0·38	2·31
40	2·99	45·0	1·67	21·9
60	4·36	120·6	3·19	70·7
80	5·02	215	4·54	148
100	5·42	320	5·71	251
120	5·66	431	6·72	375
140	5·84	546	7·60	518
160	6·00	665	8·40	679
180	6·13	786	9·11	854
200	6·24	910	9·76	1043
220	6·36	1036	10·31	1233
240	6·47	1164	10·87	1445
260	6·59	1294	11·40	1668
280	6·71	1437	11·89	1892
300	6·83	1573	12·36	2134

In reviewing thermal data up to 1948, Kelley[193] gave the following equation as representing the specific heat of solid sodium between 298 and 371° with an accuracy of ± 1%:-

$$C_p = 5{\cdot}00 + 5{\cdot}36 \times 10^{-3}T \quad (C_p \text{ in g.-cal./g.-atom, } T \text{ in } ^\circ\text{K.}).$$

Precise measurements under saturation conditions over the range 0° to 900°C. have led to the following equations for the heat capacity of solid and liquid sodium respectively:-[154] ($C_{\text{sat.}}$ in absolute joules/g.; t in °C.)

$$C_{\text{sat.}}\ (\text{solid}) = 1{\cdot}19926 + 6{\cdot}494 \times 10^{-4}t + 1{\cdot}0531 \times 10^{-5}t^2 \ (0 \text{ to } 97{\cdot}8°\text{C.})$$

$$C_{\text{sat.}}\ (\text{liq.}) = 1{\cdot}43674 - 5{\cdot}8049 \times 10^{-4}t + 4{\cdot}6229 \times 10^{-7}t^2 \ (97{\cdot}8 \text{ to } 900°\text{C.}).$$

Values calculated using these equations, for which the probable error is ± 0·3 to 0·4%, are given in Table XIV. Quenching and annealing treatments did not change the specific heat by more than 0·2%, which is within the limits of the experimental error.

TABLE XIV.- SPECIFIC HEAT, ENTHALPY AND ENTROPY OF SODIUM BETWEEN 0° AND 900°C.

Temperature °C.	$C_{\text{sat.}}$ g.-cal./g.-atom/°C.	H_T–H_0°C. g.-cal./g.-atom	S_T–S_0°C. g.-cal./g.-atom/°C.
0	6·589	0	0
25	6·838	166·2	0·582
50	6·899	333·6	1·130
75	7·182	512·5	1·655
97·80 (s)	7·493	679·6	2·120
97·80 (l)	7·608	1301	3·797
100	7·601	1318	3·841
200	7·360	2066	5·617
300	7·167	3353	7·010
400	7·026	3501	8·150
500	6·934	4198	9·116
600	6·950	4890	9·957
700	6·907	5579	10·705
800	6·969	6273	11·38
900	7·081	6975	12·01

The specific heat of solid sodium rises markedly as the melting point is approached. There is a fall on melting, and the specific heat of the liquid then decreases with increase of temperature to a minimum at about 650°C. The rise in the specific heat prior to melting is characteristic of the alkali metals.[194] Itaka,[195] who made measurements on solid sodium and on liquid sodium between 125 and 290°C., reported an increase in the specific heat on melting, but this is not borne out by the above recent work. Less precise values for the specific heat of liquid sodium at 121° and 178°C. have been obtained by measuring the adiabatic temperature-pressure coefficient.[196] A recent table[74] based on the results of Ginnings *et al.*[154] lists specific heats for liquid sodium in B.t.u./lb./°F. at 5°F. intervals between the melting point (208°F.) and 1500°F.

From the vibration frequency, Kelley[193] represented the heat capacity of diatomic sodium vapour by the equation:-

$$C_p = 8{\cdot}94 - 0{\cdot}08 \times 10^5 T^{-2} \ (\text{accuracy} \pm 0{\cdot}5\% \text{ between } 298° \text{ and } 2000°\text{K.}).$$

Values, calculated from spectroscopic data, for the heat capacity of both monatomic and diatomic sodium vapour at one atmosphere pressure are included in Table XV[179] (see page 397). Independent calculations have given very similar values.[187a]

Sodium, in common with the other alkali metals, does not obey the Debye formula, which requires a constant value for the Debye characteristic temperature, θ. Instead, θ has a value of about 90° at 2°K., 160° at 40°K. and 150°

at 120°K. Various attempts have been made to account for the deviations from the Debye theory and to calculate specific heats in agreement with experiment. Simon and Zeidler[188] suggested the existence of thermally excited quantum jumps to explain their observed behaviour, but this view has now been displaced (cf. Lithium, page 39). The generalized work of Blackman[197] showed that large variations in θ could be accounted for by a theory of specific heats which takes into account the atomic structure. Following this, Fuchs[97,98] showed that if dispersion is neglected - as is the case in the Debye theory - the anisotropy of the alkali metals gives rise to the type of divergence from the Debye formula observed with sodium. Specific heats in fair agreement with experiment have been calculated by evaluating the four discrete frequencies of atomic vibration in terms of the elastic constants of the sodium crystal, and representing the residual degrees of freedom not covered by these modes by a Debye function with a correspondingly reduced characteristic temperature.[198] More recent treatments[199,200] have been concerned also in accounting for the behaviour below 25°K., where θ falls considerably. Bauer[199] derived the frequency spectrum using a two force-constant model and from this calculated the lattice part of the specific heat as a function of temperature. Closer agreement with experiment was achieved by Bhatia[200] who derived the frequency spectrum, and hence the specific heat, using a three force-constant model. He suggests that for a metal like sodium, which is neither elastically isotropic nor in conformity with the Couchy relation $C_{12} = C_{44}$, some three force-constant model is necessary.

Characteristic temperature values have been given by a number of authors in treatments of specific heat and other data.[5,96-98,189,191,191a,192a,197-201b,205a] A recent detailed study of characteristic temperature data has used four different methods for calculating θ_D, the Debye characteristic temperature from thermodynamic data and θ_R from electrical resistance data.[201,202] At temperatures below 100°K. the various methods lead to values of about 170° for both θ_D and θ_R, but at higher temperatures the different methods give widely divergent results. Thus, while θ_D actually becomes negative above 200°K. when derived conventionally from C_v, it decreases by only 13% up to 300°K. when derived from the thermal energy.

Heat Content or Enthalpy.

Values for the heat content or enthalpy of solid and liquid sodium over the ranges 0°K.-300°K. and 0°C.-900°C. are included in Tables XIII[189] and XIV.[154] The data of Table XIV were obtained by dropping samples of sodium, sealed in stainless steel cylinders, from a constant temperature into a Bunsen ice calorimeter, and the following equations were derived from them. (Temperature is in degrees C., the enthalpy in absolute joules per g., and the estimated probable error is given as ± 0·1–0·2%.)

$$H_t\,(\text{solid}) - H_0\,(\text{solid}) = 1{\cdot}19926t + 3{\cdot}247 \times 10^{-4}t^2 + 3{\cdot}510 \times 10^{-6}t^3 \qquad (0 \text{ to } 97{\cdot}80^\circ\text{C.})$$

$$\begin{aligned} H_t\,(\text{liq.}) - H_0\,(\text{solid}) = {} & 98{\cdot}973 + 1{\cdot}436744t - 2{\cdot}90244 \times 10^{-4}t^2 \\ & + 1{\cdot}54097 \times 10^{-7}t^3 + 24{,}000\ e^{-13{,}600/t+273} \\ & (97{\cdot}80^\circ \text{ to } 900^\circ\text{C.}). \end{aligned}$$

Simplified equations based on the above data have been used to list the enthalpy of sodium in B.t.u./lb. at intervals of 5°F. between the melting point and 1500°F.[74] Other equations for solid and liquid sodium based on older experimental values are given by Kelley.[193]

For diatomic sodium vapour, Kelley[193] has given the equation:-

$$H_T - H_{298{\cdot}16} = 8{\cdot}94\,T + 0{\cdot}08 \times 10^5 T^{-1} - 2692$$

TABLE XV.- THERMODYNAMIC FUNCTIONS FOR MONATOMIC AND DIATOMIC SODIUM VAPOUR IN THEIR STANDARD STATE OF ONE ATMOSPHERE PRESSURE

T, °K.	$-\left\{\frac{F^\circ - E_0^\circ}{T}\right\}_1$ g.-cal./mole/ °K.	$-\left\{\frac{F^\circ - E_0^\circ}{T}\right\}_2$ g.-cal./mole/ °K.	$\left\{\frac{H^\circ - E_0^\circ}{T}\right\}_1$ g.-cal./mole/ °K.	$\left\{\frac{H^\circ - E_0^\circ}{T}\right\}_2$ g.-cal./mole/ °K.	S_1° g.-cal./mole/ °K.	S_2° g.-cal./mole/ °K.	C_{p1}° g.-cal./mole/ °K.	C_{p2}° g.-cal./mole/ °K.
100	26·318	37·996	4·9680	7·4871	31·286	45·483	4·9680	8·2982
298·1	31·744	46·659	4·9680	8·3331	36·712	54·992	4·9680	8·9623
371	32·831	48·496	4·9680	8·4630	37·799	56·959	4·9680	9·0233
500	34·313	51·045	4·9680	8·6181	39·281	59·663	4·9680	9·1005
800	36·648	55·146	4·9680	8·8255	41·616	63·971	4·9680	9·2369
1000	37·757	57·125	4·9680	8·9160	42·725	66·041	4·9680	9·3188
1155	38·473	58·414	4·9680	8·9742	43·441	67·389	4·9680	9·3807
1200	38·663	58·758	4·9680	8·9898	43·631	67·748	4·9680	9·3985
1400	39·429	60·148	4·9680	9·0538	44·397	69·202	4·9680	9·4771
1600	40·092	61·361	4·9680	9·1116	45·060	70·473	4·9680	9·5552
1800	40·677	62·438	4·9680	9·1652	45·645	71·603	4·9680	9·6329
2000	41·201	63·406	4·9680	9·2159	46·169	72·622	4·9680	9·7104
2200	41·674	64·287	4·9680	9·2643	46·642	73·551	4·9680	9·7879
2400	42·106	64·095	4·9680	9·3112	47·074	74·406	4·9680	9·8652
2600	42·504	65·842	4·9680	9·3568	47·472	75·199	4·9680	9·9424

Subscript (1) refers to monatomic sodium vapour.
Subscript (2) refers to diatomic sodium vapour.

as representing the enthalpy (in g.-cal./g.-mole) between 298° and 2000°K. with an accuracy of ± 0·5%. By using spectroscopic data and the methods of statistical mechanics, and by assuming the vapours to be ideal gases at a pressure of one atmosphere, the values of Table XV have been calculated[179] for the enthalpy and other thermodynamic functions of both monatomic and diatomic sodium vapour. Values calculated by Evans *et al.*[187a] in a review of the thermodynamic properties of the alkali metals are very similar.

The molecular weight, enthalpy and entropy of the equilibrium mixture of monatomic and diatomic sodium vapour at a total pressure of one atmosphere are shown in Table XVI.[179] In obtaining the enthalpy values of this Table, the zero point energies of monatomic and diatomic sodium vapour were taken as 26·05 kg.-cal./mole and 35·26 kg.-cal./mole respectively.

TABLE XVI. - MOLECULAR WEIGHT, ENTHALPY AND ENTROPY OF THE EQUILIBRIUM MIXTURE OF MONATOMIC AND DIATOMIC SODIUM VAPOUR AT A TOTAL PRESSURE OF ONE ATMOSPHERE

T, °K.	Molecular Weight g./mole	H° g.-cal./mole	S° g.-cal./mole/°K.
100	45·994	36·009	45·483
298·1	45·993	37·744	54·992
371	45·975	38·391	56·957
500	45·596	39·378	59·484
800	37·253	37·647	56·794
1000	28·849	34·366	49·785
1400	23·743	33·489	45·485
1800	23·181	35·126	45·945
2200	23·070	37·039	46·771
2600	23·036	39·001	47·543

A Mollier (enthalpy-entropy) diagram has been prepared for saturated and wet sodium vapour.[203]

Entropy.

From heat capacity data available up to 1948, Kelley[204] gave the entropy of solid sodium at 298·16°K. as 12·23 ± 0·10 g.-cal./g.-atom/°K. of which 0·09 is the extrapolation below 12·6°K. The U.S. Bureau of Standards selected value is 12·2 g.-cal./g.-atom/°K. at 298·16°K.[204] Entropy values for solid and liquid sodium at lower and higher temperatures are included in Tables XIII[189] and XIV.[154]

For monatomic sodium vapour, the Sackur equation - to which must be added $R\ln 2$ to account for the multiplicity in the lowest energy state - gives 36·72 ± 0·01 g.-cal./g.-atom/°K. for the entropy at 298·16°K.[204] The molecular constants of diatomic sodium vapour lead to $S^\circ_{298\cdot16}$ = 54·90 ± 0·10 g.-cal./mole/°K., of which 2·57 is the vibrational contribution and 52·33 the translational and rotational contribution.[204] Table XV contains values calculated from spectroscopic data for the entropy of both monatomic and diatomic sodium vapour, while Table XVI gives entropy values for the equilibrium mixture of monatomic and diatomic sodium vapour at a total pressure of one atmosphere.[179] Entropies for monatomic and diatomic sodium vapour calculated by Evans *et al.*[187a] are almost identical with those of Table XV.

Temperature-entropy and Mollier (enthalpy-entropy) charts have been constructed[203] for the system:-

$$2\text{Na(liq.)} \rightleftharpoons 2\text{Na(vapour)} \rightleftharpoons \text{Na}_2\text{(vapour)}$$

Free Energy.

Free energy data for sodium in the solid, liquid and gaseous states are included in or may be derived from the data of Tables XIII,[189] XIV,[154] XV[179] and XVI.[179]

Thermal Conductivity

Values for the thermal conductivity of solid sodium, obtained by using a modified Forbes bar method, are shown in Table XVII.[192]

TABLE XVII. - THERMAL CONDUCTIVITY OF SOLID SODIUM

Temp., °C.	−240	−200	−150	−100	−50	0	+50	+75
k (watt cm.$^{-1}$/°C.$^{-1}$)	1·69	1·58	1·42	1·28	1·17	1·40	1·21	1·13

From −240° to −40°C. there is a linear decrease in the conductivity, but between −40° and 0°C. a discontinuity occurs and the conductivity increases from 1·17 to 1·40 watt cm.$^{-1}$ °C.$^{-1}$ At higher temperatures the thermal conductivity again decreases with increase of temperature. Other measurements have been made between ~4° and 90°K.[205] and between 2° and 16°K.[205a] At temperatures below 16°K. the thermal conductivity is represented by the equation:-

$$1/k = A/T + BT^2,$$

and there is a maximum conductivity at about 4–5°K. With k in watt cm.$^{-1}$ °C.$^{-1}$ and T in °K., Berman and MacDonald[205] obtained a value of $3{\cdot}8 \times 10^{-4}$ for B, whilst A varied with the impurity content between 0·42 and 0·06. The later work[205a] gave $B = 3{\cdot}5 \times 10^{-4}$ and $A = 0{\cdot}06$–$0{\cdot}07$. Hall[206] used a guard ring method to measure the conductivity of solid and liquid sodium between 85° and 210°C.: his results for the liquid between 100° and 210°C. were represented by the equation:-

$$k = 0{\cdot}860\,[1 - 0{\cdot}338 \times 10^3\,(t - 100) - 2{\cdot}6 \times 10^6\,(t - 100)^2],$$

k being in watt cm.$^{-1}$ °C.$^{-1}$ and t in °C. Extension of the experimental curves to the freezing point gave 0·861 watt cm.$^{-1}$ °C.$^{-1}$ for liquid sodium and 1·120 watt cm.$^{-1}$ °C.$^{-1}$ for solid sodium at this temperature. The ratio of the thermal conductivities of the solid and liquid is thus 1·30, in good agreement with an older value of 1·31.[207] Employing the relationship between electrical and thermal conductivity - the Lorentz number - the thermal conductivity of liquid sodium at its melting point has been estimated as 0·23 to 0·30 g.-cal.cm.$^{-1}$ sec.$^{-1}$ °C.$^{-1}$ (0·96 to 1·25 watt cm.$^{-1}$ °C.$^{-1}$).[208] More recent measurements on liquid sodium have been made between ~180° and 510°C. and the experimental values were closely fitted by the equation $k/C_p d^{5/3}$ = constant, where k is the thermal conductivity, C_p the specific heat and d the density.[209] This equation has been used to extrapolate values up to 900°C. (Table XVIII). Thermal conductivities calculated from measurements[70a] of thermal diffusivity (= $k/C_p d$) between the melting point and 700°C. show fair agreement with the values of Table XVIII.

TABLE XVIII. - THERMAL CONDUCTIVITY OF LIQUID SODIUM

Temp., °C.	k watt cm.$^{-1}$/°C.$^{-1}$	Temp., °C.	k watt cm.$^{-1}$/°C.$^{-1}$
100	0·860[206]	600	0·631
200	0·816	700	0·600
300	0·759	800	0·573
400	0·710	900	0·552
500	0·667		

The thermal conductivity of sodium has been related to the specific heat and absolute temperature, and the lattice and atomic contributions to the thermal conductivity at 0°C. are given as 0·092 and 0·169 g.-cal.cm.$^{-1}$sec.$^{-1}$ °C.$^{-1}$ respectively.[210] Several authors[205,210a–c] have discussed the discrepancies between experimental values for the thermal conductivity of sodium at low temperatures and the predictions of the electron theory of metals.

Thermal conductivities have also been reported for sodium amalgams containing 70 to 94 atoms % Na[206] and for sodium–potassium alloys.[70a,72,211]

The high thermal conductivity of sodium - coupled with other properties such as its reasonably low melting point and low vapour pressure even at fairly high temperatures - gives the metal very useful heat transfer properties. Its Prandtl number, *i.e.* the product of the specific heat at constant pressure and the viscosity divided by the thermal conductivity, is 0·0072 at 200°C. and 0·0038 at 700°C.[72] Heat transfer coefficients for liquid sodium have been studied recently, especially in connexion with the use of liquid sodium as a heat transfer medium for developing power from nuclear reactors.[212-214] In general reviews of this field[212-213] numerous references to other work are given. Sodium–potassium alloys have lower thermal and electrical conductivities than sodium but they are nevertheless useful as heat transfer media since they are liquid at room temperature. Sodium itself appears to be the most suitable coolant for nuclear power reactors.[215]

Electrical Resistance

Bidwell[192] determined the specific resistance of sodium at 0°C. to be $0{\cdot}426 \times 10^{-5}$, and combining this figure with his earlier measurements of relative resistance[216] he obtained the following values for specific conductance:-

Temp., °C.	−240	−200	−150	−100	−50	0	50	75
σ, ohm^{-1}cm.$^{-1}$ × 10^{-4}	226·0	133·3	67·0	43·4	31·4	23·5	18·9	17·1

There is a marked increase in the electrical resistance as the melting point is approached[216] (Fig. 3). This and the similar rise in specific heat on approaching the melting point (see page 395) have been discussed in terms of lattice defects.[216a] Using sodium produced by electrolysis through glass, Nielsen[217] found the specific resistance of the solid at 30–90°C. to be given by: $4661 \times 10^{-9} \times (1 + 0{\cdot}00484t)$ and that for the liquid below 160° by $9828 \times 10^{-9} \times (1 + 0{\cdot}00354(t - 100) + 0{\cdot}00000039(t - 100)^2)$. Woods,[205a,217a] who made measurements in the region 4° to 15°K. on samples of sodium for which the residual resistivity was $1{\cdot}38 \times 10^{-9}$ ohm cm., found that after subtracting the residual resistivity the 'ideal' resistivity was given by

$$\rho = 8{\cdot}6 \times 10^{-16} T^6 \text{ ohm cm. between } 4^\circ \text{ and } 9^\circ\text{K.}$$

and by $$\rho = 8{\cdot}4 \times 10^{-15} T^5 \text{ ohm cm. between } \sim 8^\circ \text{ and } 15^\circ\text{K.}$$

From other measurements[205] on samples with residual resistivities of 10^{-8} to 10^{-9} ohm cm. the 'ideal' resistivity below 15°K. was represented by

$$\rho = 5{\cdot}37 \times 10^{-15} T^5 \text{ ohm cm.}$$

Several other workers have measured the resistance of sodium at low temperatures relative to that at 0°.[218-221] Woltjer and Onnes[218] obtained $R/R_{273°\mathrm{K}} = 0{\cdot}5672$ at 170·87°K., 0·3168 at 108·72°K. and 0·1055 at 56·77°K. It was found by Meissner and Voigt,[219] who made measurements down to 1·23°K., and by MacDonald and Mendelssohn,[221] who made continuous measurements over the range 1·5° to 20°K., that below liquid helium temperature (4·2°K.) the resistance was substantially constant. The magnitude of the 'residual' resistance is an indication of the purity of the samples used.

Meissner and Voigt obtained a residual resistance of $R/R_{273^\circ K.} = \sim 3 \times 10^{-3}$, while MacDonald and Mendelssohn using a purer sodium sample obtained $\sim 7 \times 10^{-4}$. It is customary in calculating R/R_{273° values to subtract the residual resistance: when this is done the results of the various workers are in close accord. Thus at 20·4°K. the investigations cited give $R/R_{273} = 0{\cdot}0034_7$[219] and 0·00326.[221] Table XIX contains some values of low-temperature resistance ratio corrected for residual resistance.

TABLE XIX.- RELATIVE ELECTRICAL RESISTANCE OF SODIUM AT LOW TEMPERATURES

Temp., °K.	4·2	8·1	9·65	11·05	13·1	14·1
$R/R_{273^\circ K.}$	0·00000[221]	0·00005[221]	0·000 10[221]	0·000 17[221]	0·00036[221]	0·00051[221]
Temp., °K.	15·95	20·4	77·6	87·8	90·0	
$R/R_{273^\circ K.}$	0·00098[221]	0·000326[221]	0·1849[219]	0·2279[219]	0·2420[221]	

Kamerlingh Onnes and co-workers[222,223] showed that sodium was not superconducting down to a temperature of 1·5°K., and later work[224,225] has shown that this is also true down to 0·09°K.

Kapitza[226] found that the application of a transverse magnetic field of 300 kilogauss increased the resistance of a sodium wire by 7% at 90°K. and by less than 2% at room temperature. A more detailed study of the effect of transverse and longitudinal fields on the electrical resistance of sodium has been made by Justi[220,227] who used field strengths up to 40 kiloguass at temperatures between 14° and 78°K. Percentage resistance increases of up to 50% were observed on applying the field.[220]

Resistivity measurements on very pure sodium in capillaries with diameters between 15 and 66μ and at temperatures between 20 and 4·2°K. have shown a size-effect, the resistivity increasing with decreasing diameter of the wire.[228] It has also been found recently that under these conditions application of transverse and longitudinal magnetic fields produces a decrease in the resistivity: for large longitudinal fields the resistivity tends towards its bulk value.[228,229] The conditions for this effect are such that the diameter of the specimen, the free path of the conduction electrons, and the radius of the circular orbits of the electrons in the magnetic field are all of comparable orders of magnitude. This behaviour, which contrasts with that in the bulk material where magnetic fields cause increases in resistivity, has been treated theoretically.[230-232]

Earlier measurements (Mellor,II,460) of the effect of pressure on the electrical resistance of sodium have been extended to higher pressures.[233,234,430] Table XX shows values to 100,000 kg./cm.².[430] A very flat minimum occurs in the curve in the region of 45,000 kg./cm.²

TABLE XX.- EFFECT OF PRESSURE ON THE ELECTRICAL RESISTANCE OF SODIUM

Pressure,kg./cm.²×10⁻³	0	10	20	30	40	50	60	70	80	90	100
R/R_0	1·0	0·618	0·483	0·413	0·392	0·390	0·399	0·412	0·430	0·452	0·479

A wave-mechanical view of the effect of pressure on the electrical resistance of sodium has been given by Frank.[235]

Calculations of the electrical resistance of sodium based on electronic theories of metallic conduction have, in general, shown fairly close agreement with experiment.[236-239] The temperature coefficient of resistance[237,240] and the change of resistance on melting[240] have also been treated mathematically.

Thermoelectric Properties

Bidwell[216] measured the thermoelectric power of sodium relative to platinum between −180° and +150°C. His results are shown in Fig. 3. Above −40°C. the thermoelectric power-temperature curve deviates from the straight line which it follows from −180°C. There is a marked increase in thermoelectric power as the melting point is approached; thereafter it decreases with rise of temperature.

The thermoelectric force of sodium against lead down to 4·2°K. was studied by MacDonald and Pearson,[241,242] who converted their values to the absolute e.m.f. scale using the absolute thermoelectric force of lead measured by Borelius *et al.*[243] Resultant values for the absolute thermoelectric force of sodium (interpolated from their graphically presented results) are:-

T, °K.	0	10	20	30	40	50	60	70	80
Microvolts	0	0	−7	−18	−33	−52	−74	−96	−120

Down to ~15°K. the thermoelectric power is directly proportional to the temperature, but at lower temperatures there are indications of a trend to a higher power law.[241] The thermoelectric effect of the alkali metals has been discussed from the viewpoint of the electron theory of metals.[241,242,244]

Magnetic Properties

Sodium, like the other alkali metals, is paramagnetic and its susceptibility varies only slightly with temperature. More recent determinations have given values for the mass susceptibility rather higher than that, 0·51 × 10^{-6}, quoted previously (Mellor,II,460). Using the Gouy method, Lane and Bieler[245] obtained 0·65 × 10^{-6} for the mass susceptibility at room temperature. The value remained constant for field strengths between 8 and 12 kilogauss showing the sample to be free from ferromagnetic impurity. Other workers[246] obtained 0·63 × 10^{-6} for the mass susceptibility of sodium at room temperature, and practically the same value was found at liquid air temperature. Klemm and Hauschulz[247] obtained 0·66 × 10^{-6} at ordinary temperatures. Recently, Bowers,[248] also using the Gouy method, found the mass susceptibility at room temperature to be 0·70 × 10^{-6} ± 0·03 × 10^{-6} and observed that the susceptibility decreased by 4·5% between room temperature and 55°K. Sucksmith[249] found 0·62 × 10^{-6} for the mass susceptibility at 500°C. Bohm and Klemm[9] have given the following values for the atomic susceptibility (mass susceptibility × atomic weight) of sodium between −183 and +100°C.:-

T, °C.	−183	−78	+20	+100
$\chi_{At} \times 10^6$	15·2	15·4	15·6	16·4

Theoretical computations of the susceptibility of sodium agree fairly well with experiment.[250-252] Samson and Seitz,[252] on the basis of the electronic structure, calculated the volume susceptibility to be 0·70 × 10^{-6} made up as follows: spin paramagnetism, 1·11 × 10^{-6}; free electron diamagnetism, −0·23 × 10^{-6}; ion core diamagnetism, −0·18 × 10^{-6}. A recent correction[253] has slightly increased the free electron diamagnetism term, but has little effect on the nett susceptibility. Electron spin resonance absorption has been observed in bulk and dispersed sodium.[130a-b,253a-c] Line shapes and width, relaxation times, and splitting factors have been determined. That part of the volume susceptibility arising from conduction electron spin was calculated by Pines[253d] to be 0·85 × 10^{-6}c.g.s. units.

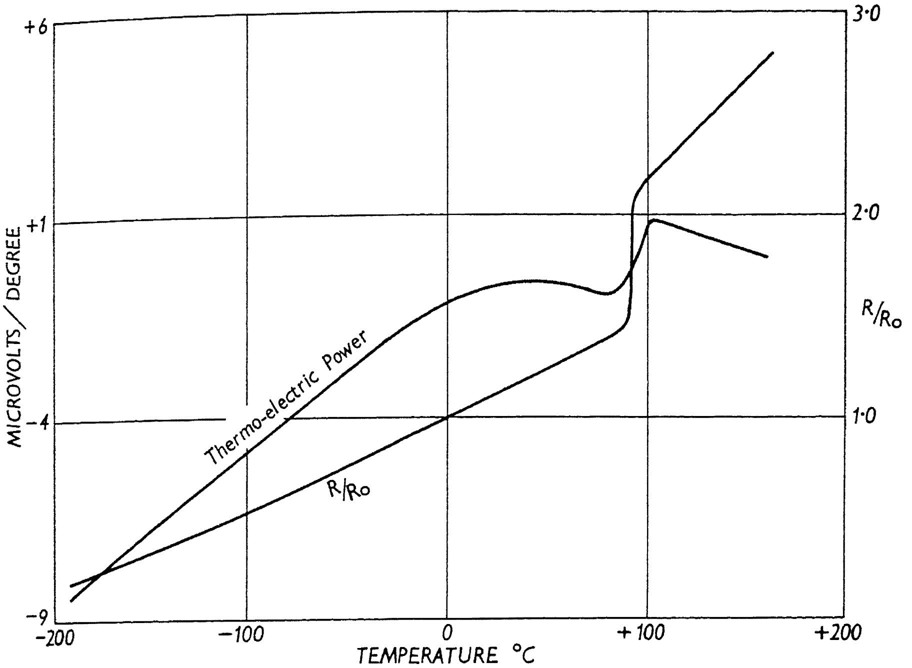

FIG. 3. RELATIVE RESISTANCE AND THERMOELECTRIC POWER CURVES FOR SODIUM

Numerous authors have attempted to evaluate the contribution of the sodium ion to the diamagnetism of its salts either by making use of experimental data for the salts or by applying theoretical methods. The various treatments have, however, given widely differing values. Values for the susceptibility of the sodium ion in solution obtained from measurements on its salts include -10·4,[254] -8·5,[255,256] -7·7,[257,258] -7·0,[259] -5·6[260,261] and -5·2[262] (all to be multiplied by 10^{-6}), while values for the Na^+ ion in crystals include -7·6 × 10^{-6} [263] and -6·1 × 10^{-6}.[264,265] Theoretical treatments have given the following values for the free Na^+ ions: -15·0,[266] -10·89,[267] -10,[268] -7·9,[269] -5·47,[270] -5·05,[271] -4·2,[262,272,273] -4·1,[265] -3·74,[274] -2·9[275] (all to be multiplied by 10^{-6}). Other values for the free ion include -9·0,[255,256] -8·2[257,258] and -7·5[259] (all to be multiplied by 10^{-6}). Klemm[276,277] in a review of the field has given -2·3 × 10^{-6} as the most probable value for the susceptibility of the Na^+ ion in solution, -4·6 × 10^{-6} for the Na^+ ion in crystals and -5·0 × 10^{-6} for the free Na^+ ion. Another contemporary survey[278] recommends -6·8 × 10^{-6} for the Na^+ ion but does not distinguish between the ion in solution and in crystals.[279] Methods of obtaining ionic susceptibilities and/or the values which have resulted from them have been reviewed by several authors.[276,278,280-282]

By passing a beam of sodium atoms through a non-homogeneous magnetic field, as in the classical experiments of Stern and Gerlach, sodium is found to have a magnetic moment of 1 Bohr magneton.[283-285] The behaviour of a beam of alkali atoms when passed through a rotating magnetic field has been examined both experimentally[286] and theoretically.[287,288] The best values for the magnetic moment of the ^{23}Na nucleus lie between 2·215 and 2·217 nuclear magnetons;[289-291] other values vary between 2·08 and 2·6 nuclear magnetons.[292,293]

Nuclear magnetic resonance and the nuclear moment of ^{23}Na have been studied and discussed by a number of other authors.[140–141b,294–306] Knight[301] found that the nuclear magnetic resonance frequency of sodium in the metallic state was about 0·1% higher than that of sodium in its salts. At room temperature the resonance frequency of sodium in its salts at the field used was 10·123 Mc./sec. and the frequency shift in the metal was 10·5 Kc./sec. The shift has been attributed to the interaction of the magnetic moment of the nucleus with the magnetic moments of the conduction electrons.[302] Between 75° and 25°K. the frequency shift has been observed to drop by about 10% of its value at 300°K.[305]

The spin of the ^{23}Na nucleus has a value of 3/2.[293,307,308]

Electrode Potentials

The chemical reaction between sodium and water prevents a direct determination of the standard electrode potential of sodium. An indirect method due to Lewis[309] may be employed, however. This involves measuring the potential difference of two cells:-

(a) Pure sodium against a dilute sodium amalgam when both are immersed in a solution of sodium ions in a non-aqueous solvent inert towards sodium.

(b) The dilute amalgam in an aqueous sodium salt relative to a calomel or other reference electrode.

The European convention regarding the sign of the electrode potential is followed in all the values below. A recalculation[310] of the results of Lewis and Kraus,[309] who used:-

Na (solid) | NaI in ethylamine | Na (0·206% amalgam)

as their non-aqueous cell, has given -2·7126 V. for the standard electrode potential of sodium at 25°C. on the hydrogen scale. More recent measurements by Smith and Taylor[311] on the cells:-

Na (solid) | NaI in dimethylamine | Na (0·0651% amalgam) and

Na (0·0651% amalgam) | NaCl (0·05 or 0·1 M.); AgCl (solid) | Ag (solid)

between 5 and 40°C. have led to the expression:-

$$E^{0}_{\mathrm{Na}} = -2{\cdot}71324 - 0{\cdot}7532 \times 10^{-3}\,(t - 25) - 0{\cdot}688 \times 10^{-6}\,(t - 25)^2.$$

Trümpler[312] has developed a glass-membrane sodium electrode, and from measurements on the cell:-

Na | Glass | NaCl (satd. soln.) | Reference electrode

has obtained -2·72 V. for the sodium standard potential. The sodium/glass electrode has also been studied in fused salts,[313,313a] and a sodium/sodium chloride (solid) electrode has been studied in aqueous solution.[312] More recent measurements[314] of sodium amalgam potentials obtained by a glass membrane technique have been combined with the values of Bent and Swift[315] (see below) for the activity of sodium in amalgams to give -2·7109 ± 0·0005 V. for the standard potential of sodium. Thermodynamic calculations of the standard potential have been made by Drossbach[316–318] who finally arrived at E^{0}_{Na} = -2·72 V. From measurements of the decomposition voltages of fused sodium halides, a value of -2·454 V. has been given for the potential of sodium at 18°C.[319] The determination of the absolute electrode potential of sodium has been discussed,[320,321] and using spectroscopic and thermodynamic data, Gapon[321] has calculated its value as +1·18 V.

The best representative values for the standard electrode potentials of the alkali metals in aqueous solution at 25°C. are compared below:-[322]

Lithium	-3·01 V.
Sodium	-2·713 V.
Potassium	-2·92 V.
Rubidium	-2·92 V.
Cæsium	-2·92 V.

Sodium is seen to have the least negative potential of the alkali metals.

A value of -0·39 V. has been calculated for the potential of the ionic double layer at sodium which leads to -2·32 V. for the potential of zero charge or of the maximum of the electrocapillary curve.[322a]

In most non-aqueous solvents the standard electrode potential of sodium is less negative than in water. The standard potential at 25°C. (relative to $E^{\circ}_{\mathrm{H}_2} = 0$ in the respective solvent) is -2·728 V. in methyl alcohol[323] and -2·657 V. in ethyl alcohol.[324] Koch[325] made measurements on cells of the type:

Na amalgam | NaI in pyridine, NaI in other solvent | Na amalgam

where 'other solvent' represents a variety of liquids including water. Taking the standard potential of sodium in water as -2·713 V. the following standard potentials (relative to $E^{\circ}_{\mathrm{H}_2} = 0$ in water) were derived for other solvents:-

Methyl alcohol	-2·551 V.	Acetone	-2·472 V.
Pyridine	-2·478 V.	Ethyl cyanoacetate	-2·408 V.
Ethyl alcohol	-2·477 V.	Propionitrile	-2·404 V.
Acetonitrile	-2·474 V.	Benzonitrile	-2·357 V.

In nitrobenzene the standard potential has been given as -2·545 V.,[326] and in ethyl bromide it is -2·45 V.[327] Other measurements of the sodium electrode potential have been made in liquid ammonia,[328-331] hydrazine[332] and formic acid.[333] The electrode potentials of the alkali metals in these last three solvents and in water have been compared in Table XII on page 47.

Relative values for the electrode potentials of sodium and other metals in various fused halide electrolytes have been obtained by direct measurement or by calculation from thermodynamic data, and electrochemical series have been developed.[313a,333a-c] The order of the metals in the series varies with the anion and with the temperature, and in the case of mixed salts it may also be affected by complex formation. The difference in potential between sodium and the heavy metals decreases along the anion series: chloride, bromide, iodide.

Some measurements of the potential of sodium amalgam electrodes have been referred to above in arriving at the standard potential of sodium;[309,311,314,315] a number of other studies of sodium amalgam electrodes have also been made.[334-341] Many of the investigators have, however, worked only with a single, low, sodium concentration. Trümpler *et al.*,[314,341] using the glass membrane technique, made measurements at sodium concentrations between 0·0005 and 0·6%: the following potentials (on the hydrogen scale) are for amalgam electrodes at 25°C. in a sodium ion solution of unit activity:-[314]

% Na	0·0091	0·0138	0·0240	0·0352	0·0453
Amalgam Potential, (volts)	-1·770	-1·781	-1·797	-1·807	-1·815
% Na	0·0563	0·0865	0·1460	0·2579	
Amalgam Potential, (volts)	-1·821	-1·835	-1·853	-1·876	

Potentials obtained by the glass membrane technique have been found to be several millivolts more positive than those obtained by a direct method. Smith and Taylor,[311] using a direct method, obtained -1·828 V. on the hydrogen scale for the potential at 25°C. of a 0·0651% sodium amalgam in a Na^+ ion solution of unit activity. Older direct measurements on amalgam electrodes in normal Na^+ ion solutions at 25°C., all made relative to a normal calomel electrode, have included -2·1430 V. for 0·1389% Na,[334] -2·1549 V. for 0·194% Na[337] and -2·1525 V. for 0·206% Na.[309] Bent and Swift,[315] from potential measurements on sodium amalgam concentration cells in non-aqueous media expressed the activity of sodium in dilute amalgams by the following equations:-

$$\log a/N \text{ (25°C.)} = -12{\cdot}81441 + 15{\cdot}6130N + 7{\cdot}530\,N^2$$
$$\log a/N \text{ (15°C.)} = -13{\cdot}32030 + 15{\cdot}87260N + 7{\cdot}110\,N^2$$
$$\log a/N \text{ (5°C.)} = -13{\cdot}86807 + 16{\cdot}1820N + 5{\cdot}970\,N^2$$

where a is the activity of sodium in the amalgam and N is its mole fraction. Combination of these three equations has given:-

$$\log a/N = \frac{-8387{\cdot}6}{T^{1{\cdot}138}} + \frac{338{\cdot}2\,N}{T^{0{\cdot}54}} + 7{\cdot}0\,N^2$$

Activities of sodium in solid amalgams have also been studied.[342] At concentrations up to about 0·1% of sodium, the potential of a sodium amalgam electrode gives approximately a linear plot against the logarithm of the sodium concentration, but at higher concentrations there is a deviation from this line.[341]

Measurements of the potential of amalgam cathodes during the deposition of sodium from concentrated sodium chloride solutions have been reported.[343-345]

The behaviour of sodium ions at the dropping mercury electrode was studied by Heyrovsky[346,347] in his first polarographic experiments; he gave the deposition potential of sodium at mercury from aqueous solutions as -1·860 V. relative to a normal calomel electrode. Other more recent studies have been made in both aqueous and non-aqueous media. Despite the very negative standard potential of sodium, its ions are discharged at a mercury cathode in neutral and alkaline solutions without simultaneous discharge of hydrogen ions because of (*a*) compound formation between mercury and sodium reducing the discharge potential of the sodium ions, and (*b*) the high hydrogen overvoltage at mercury causing the discharge potential for hydrogen ions to be much higher than the reversible hydrogen potential. The negative potential does, however, limit the choice of supporting electrolyte; tetra-alkyl ammonium halides or hydroxides are virtually the only usable salts.[348] With tetramethylammonium chloride or hydroxide as the supporting electrolyte, the half-wave potential of sodium ions in aqueous solution is -2·15 V. relative to a normal calomel electrode.[349,350] More precise studies in a 0·1 M-tetramethylammonium hydroxide solution at 25°C. have given the half-wave potential as $-2{\cdot}142_5$ V. against a normal calomel electrode;[350a-b] the value extrapolated to zero concentration of the supporting electrolyte was the same within the limits of experimental error. Diffusion waves for sodium ions in alcohol–water mixtures are better developed than those in purely aqueous solutions.[351-353] In 50% ethyl alcohol at 25°C., with 0·1 M-tetraethylammonium hydroxide as the supporting electrolyte, the half-wave potential of sodium is -2·07 V. relative to a saturated calomel electrode: in 80% ethyl alcohol it is -2·035 V.[352,353] Sodium has a half-wave potential so close to those of potassium (-2·10 V.), rubidium (-1·99 V.) and cæsium (-2·05 V.) (all in 50% ethyl alcohol + 0·1 M-tetraethylammonium hydroxide) that these four elements cannot be differentiated polarographically.[348] In the presence of colloidal materials such as gelatin and agar agar the deposition potentials of the alkali metals at a dropping mercury cathode tend to become less negative.[354] Polarographic waves in ethylene glycol, trimethylene glycol, glycerol and in dioxan–water mixtures have also been studied.[351] At −36°C., in liquid ammonia saturated with tetrabutylammonium iodide as supporting electrolyte, the half-wave potential of the sodium ion relative to a 0·1 N-Pb/$Pb(NO_3)_2$ reference electrode is −1·31 V.[355]

Using an oscillographic method, Heyrovsky[356] has shown that when a dropping mercury electrode is subjected to alternate cathodic and anodic polarization at a frequency of 50 cycles per second, the cathodic and anodic depolarization processes occur at the same potential.

Ionization Potentials, Electron Affinity and Electronegativity

Ionization potentials of sodium have been calculated from spectral series limits. Values, in electron volts, from two recent compilations are:-

I	II	III	IV	V	VI	VII	VIII	IX	Reference
5·138	47·29	71·65	98·88	138·60	172·36	208·444	264·155	299·78	357
5·14	47·3	71·7	98·9	138·6	172·5	209·1	264·3	299·9	358

By extrapolation along the isoelectronic sequences, the tenth ionization potential of sodium has been estimated as 1460[358] and 1465 e.V.,[359] while the eleventh ionization potential has been estimated as 1646 e.V.[359]

Thermal ionization of sodium vapour occurs at high temperatures.[360-363] Ionization of sodium and other alkali metal vapours on hot surfaces of tungsten, molybdenum and other metals has attracted the attention of a number of workers.[364-371a]

Quadratic extrapolations from the ionization potentials of isoelectronic species have led to estimates of +0·08,[372] 0·0[373] and −0·08 e.V.[374] for the electron affinity of sodium: the last value is based on the latest spectroscopic data. It has been suggested[373] that electron affinities obtained by the above procedure are to be regarded as lower limits. A linear extrapolation method,[375] which in general yields less satisfactory values, has given +1·1 e.V. for the electron affinity. Hartree and Hartree,[376] using the consistent-field method, calculated wave functions for the negative Na^- ion and deduced that not only can this ion exist but also it is probably stable. A more recent and improved calculation of the electron affinity has given +1·2 e.V. confirming the stability of the Na ion.[377] Such ions have been reported from mass spectrometer studies.[378]

Sodium has a value of 0·9 on Pauling's electronegativity scale, values for the other alkali metals being Li, 1·0; K, 0·8; Rb, 0·8 and Cs, 0·7.[61] As pointed out by Mulliken,[379] the sum of the first ionization potential and the electron affinity when divided by 130 gives values in close agreement with Pauling's electronegativities for sodium and for other atoms.[61]

Optical and Photoelectric Properties

Thin films of the alkali metals are opaque to visible light, but they are highly transparent in the ultra-violet region of the spectrum.[380] The wavelength at which sodium ceases to exhibit the optical properties of a metal and acquires those of a transparent medium is about 2100 A.[380] No renewal of reflecting power in the far ultra-violet has been found down to 500 A.[381] A film of sodium on fluorite can be used as a filter to remove all visible and ultra-violet light of wave-length greater than 2100 A. and to pass the entire Schumann region of the spectrum.[382] In the transparent region, sodium yields plane polarized light by reflection of non-polarized light at an angle in accordance with Brewster's law.[380]

Ives and Briggs[383] studied the reflection of monochromatic plane polarized light from sodium surfaces, and from their results calculated the refractive index (n), the extinction coefficient for normal incidence (K_0), the reflecting power for normal incidence (R), the principal angle of incidence ($\bar{\phi}$) and the principal azimuth ($\bar{\psi}$). Values for these are given in Table XXI.

In an earlier measurement of the optical constants of sodium, Morgan,[384] using light of wave-length 5461 A., obtained 0·047 for the refractive index, 47·3 for the index of absorption and 96·9 for the reflecting power.

TABLE XXI. - OPTICAL CONSTANTS OF SODIUM

λ, (A.)	n	K_0	R (%)	$\bar{\phi}$	$\bar{\psi}$
5780	0·027	2·59	98·6	71° 4′	45° 16′
5461	0·029	2·32	98·2	69° 27′	45° 18′
4358	0·048	1·80	95·6	65° 41′	45° 26′
4047	0·048	1·56	94·5	63° 34′	45° 40′
3650	0·042	1·44	94·7	62° 21′	45° 36′
3126	0·040	1·02	92·6	57° 31′	45° 40′
2652	0·028	0·735	93·1	53° 34′	45° 29′
2536	0·026	0·621	92·7	51° 52′	45° 28′

A number of theoretical treatments of the optical properties of solid sodium have appeared, particular attention having been paid to the explanation of the transparency in the ultra-violet region.[385-391c] Zener,[386] using the free electron gas model, calculated the approximate values of the critical wave-lengths at which sodium and the other alkali metals become transparent to ultra-violet light.

Scattering of light from perfectly clean surfaces of liquid sodium has been studied.[392] The scattering is attributable to surface irregularities resulting from thermal agitation, and can be related to the surface tension of the liquid.

In the vicinity of the yellow D-lines (5890 A. and 5896 A.), sodium vapour exhibits 'anomalous' or selective dispersion. The variation of the refractive index with wave-length in the vicinity of these lines has been investigated by Stewart and Korff[393,394] who made measurements from 5830 A. to 5960 A. at several vapour densities. Fraser[395] was unable to detect any change in the refractive index of sodium vapour when measured with and without an applied magnetic field. Magnetic double refraction (Voigt effect) in the vapours of sodium and other alkali metal vapours has been studied by Gabler[396] who followed the variation of the effect with the vapour pressure of the metal.

Light falling on the surface of sodium liberates conduction electrons with an efficiency (expressed as:- number of electrons emitted/number of incident photons) that is dependent on the wave-length of the light and on the state of the sodium surface. For pure sodium films (deposited on aluminium) the efficiency has been found to be zero for light of wave-length greater than 5150 A. (having an equivalent photon energy of 2·4 e.V.).[397] From this threshold the efficiency increases steadily with decreasing wave-length to a maximum in the ultra-violet. For smooth (specular) surfaces prepared by rapid evaporation, the maximum, which has a value of $\sim 5 \times 10^{-4}$, is very flat and lies between 2000 and 3000 A.[398] Matt surfaces prepared by slow evaporation show a much sharper maximum of $\sim 4 \times 10^{-3}$ at a wave-length around 3000 A. These measurements are all for light at normal incidence: increasing the angle of incidence increases the maximum efficiency for both smooth and matt surfaces.[398] For smooth surfaces the efficiency with light at an angle of incidence of 60° is three or four times that at 0°, while for matt surfaces the efficiency at 70° is almost double that at 0°.[398]

For very thin layers of sodium ($\lesssim$ 1 molecule thick) the substrate affects the observed photoelectric effect,[399] but for thicker layers the effect becomes characteristic of sodium, though the efficiency continues to increase with film thickness up to a limiting value reached at about 80 molecular layers.[397] This thickness is much greater than that for other alkali metals where the maximum sensitivity is reached with films of about 10 molecular layers. Thick sodium layers exposed to artificial mean noon sunlight have been reported to yield 0·095 to 0·44 microamp. per lumen.[400] Ives and Olpin[401] studied the variation of the photoelectric threshold for thin sodium films as a function of film thickness. With increasing thickness the threshold moved towards the red end of the spectrum, and after reaching an extreme position receded to the value for thick films. The wave-length of maximum excursion of the threshold into the red (~5900 A.) was found to be very similar to the wave-length of the first line of the principal series (5896 A.).

Burt,[402] who prepared a pure sodium surface by electrolysis through a soda-glass tungsten filament lamp immersed in fused sodium nitratemreported that the photoelectric efficiency to white light was largely independent of temperature between - 190° and 20°C. Ives and Johnsrud[403] found little variation in the photoelectric efficiency over this temperature range when using white or blue light, but with yellow light the efficiency decreased considerably with decreasing temperature, the value at - 180°C. being approximately 65% of that at 20°C. For white and blue light there was actually a very flat maximum in the efficiency-temperature curve at intermediate temperatures in the neighbourhood of -80°C.[403]

The presence of impurities in sodium surfaces usually increases the photoelectric threshold and causes the efficiency to show one or more pronounced maxima at visible or near ultra-violet wave-lengths (see Fig. 4). Both these effects lead to an increase in the efficiency to white light. This 'spectral selectivity' is also associated with 'polarization selectivity', the efficiency depending on the polarization of the light and usually being greatest when its E vector is in the plane of incidence.[404,405] Olpin[406] studied the effect of a large number of impurities on sodium photocells and found that those enhancing the sensitivity included air, oxygen, hydrogen, water vapour, sulphur vapour, sulphur dioxide, hydrogen sulphide, sodium bisulphite, carbon disulphide, methyl alcohol, acetic acid, benzene, nitrobenzene, acetone and some organic dyes such as tropaeolin, eosin, cyanine, kryptocyanine, dicyanine and neocyanine. Deposition of a thin film of sodium on a sodium surface already treated with sulphur vapour resulted in a further twofold increase in sensitivity. An even greater.increase was brought about by admitting air to a sodium surface already treated with sulphur and then depositing a thin film of sodium on this. The sensitivity of the resultant NaS–air–Na surface extended to 10,000 A. Such treatments can produce cells with sensitivities as high as 7 microamp. per lumen for white light of colour temperature 2848°K.[406] The amounts of impurity required for sensitization are very small: the optimum amount of sulphur is $\sim 4 \times 10^{-7}$ g.cm.$^{-2}$,[407] and of oxygen $\sim 6 \times 10^{-7}$ g.cm.$^{-2}$.[408] Distillation of sodium in air at a pressure of several mm. of mercury results in a grey surface with a high photoelectric efficiency (Fig. 4).[409]

It has long been known[410] that the passage of an electric discharge through a low pressure of hydrogen in contact with an alkali metal results in an increase in the photoelectric sensitivity of the metal. More recent work has shown, however, that no sensitization occurs if the hydrogen is dried, and that helium plus water vapour are as effective as moist hydrogen.[411] It is quite possible that minute traces of some common impurity may be responsible for other sensitization processes among those cited above.

Absorption of light in sodium vapour from the series limit at 2412 A. to about 1600 A. has been studied by Ditchburn *et al.*[411a,b] The atomic absorption cross section at the limit was $11{\cdot}6 \times 10^{-20} \pm 1{\cdot}2 \times 10^{-20}$ cm.^{2} and it had a minimum value of $1{\cdot}3 \times 10^{-20} \pm 0{\cdot}06 \times 10^{-20}$ cm.^{2} at 1900 A. A theoretical treatment by Seaton[411c] has reproduced the main features of the experimental results.

Miscellaneous Physical Properties

The chemical constant of sodium has been discussed by a number of authors.[155,173,186,412–414a] From the vapour pressure measurements of several workers, Ladenburg and Thiele[155] gave the best value of the chemical constant as 0·78 ± 0·1. Other more recent calculations have given 0·83 ± 0·1.[414a]

Empirical methods for the estimation of critical constants have given values of 1960°K. and 2550°K. for the critical temperature of sodium and 363 atm. and 300 atm. for the critical pressure.[203]

Independent measurements of the velocity of ultrasonic waves (12 Mc.) in liquid sodium at its melting point have given values of 2526 ± 5 m./sec. (temperature coefficient = −0·524 ± 0·003 m./sec./°C. between the melting point and 272°C.)[89] and 2395 ± 25 m./sec. (temperature coefficient = approximately −0·3 m./sec./°C. between the melting point and 235°C.).[90]

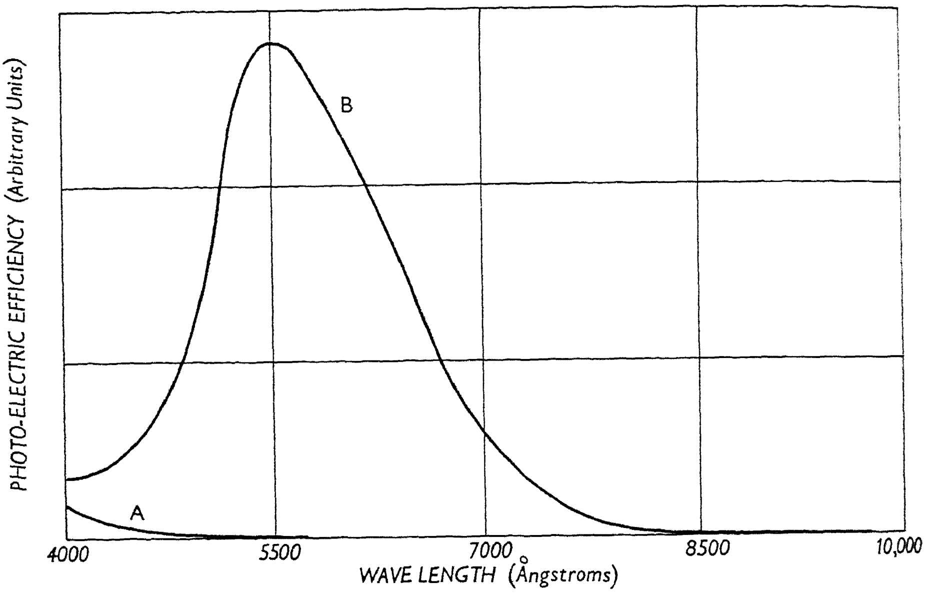

FIG. 4. SPECTRAL SENSITIVITY OF SODIUM SURFACES
A. DISTILLED IN VACUUM
B. DISTILLED IN AIR AT A PRESSURE
OF 1·5 MM. MERCURY

Studer and Williams,[415] using carefully purified sodium specimens, obtained −0·0021 for the Hall constant of sodium. More recently, Justi,[220] who made measurements from room temperature down to 0·73°K. and found the Hall constant to be substantially independent of temperature and field strength, has given the following values: −0·00127 at 20·4°K., −0·00124 at 78°K., and −0·00132 at 300°K. Calculated values of the Hall constant of sodium have included −0·00246[416] and −0·00245.[417]

Measurements of the contact potential difference between sodium and other surfaces have included the following values: sodium against molybdenum, 2·05 V.,[418] 2·0 V.;[419] tungsten, 2·2 V.;[419] iron, 1·4 V.;[419] nickel, 2·45 V.;[419] platinum, 2·1 V.,[419] 2·39 V.;[420] copper, 2·05 V.[419] When a tungsten filament is cleaned and exposed to sodium at a fixed pressure the work function falls to a minimum and then rises slowly to a final steady value.[421] The contact potential of the film of minimum work function against clean tungsten has been measured as 2·78 V.[421]

The photoelectric threshold for a clean sodium surface (see page 409) leads to a value of 2·4 e.V. for the work function. Theoretical values for the work function of sodium have included 2·15 e.V.[422] and 2·11 e.V.[423] From potential measurements on amalgam systems, Klein and Lange[424] obtained electron work functions for a large number of metals, their value for sodium being 1·60 e.V.

A method for detecting the level of liquid sodium in stainless steel tubes has been described.[425] It utilizes the change of inductance of a narrow coil of wire wound round the tube, and succeeds because the tube is only feebly magnetic and the liquid metal is a good conductor.

Sodium and its salts do not exhibit any natural radioactivity.[426-429]

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PROPERTIES OF THE SODIUM ION

Some properties of the sodium ion, and some properties that relate to both the metal and its ion, have been dealt with under the appropriate sections above. Other properties of the Na^+ ion will be considered here.

The Ion in Solution

The heat and free energy of formation of the aqueous sodium ion at 25°C. are $-57{\cdot}279$ and $-62{\cdot}589$ kg.-cal.g.-ion^{-1} respectively.[1] The absolute heat capacity of the Na^+ ion at infinite dilution has been calculated from measurements on various aqueous salt solutions;[1a,b] assuming equal values for the heat capacities of the NH_4^+ and Cl^- ions, that of the Na^+ ion has been given as $-15{\cdot}0$ g.-cal./degree/g.-ion.[1a] From thermal data for the three ionizaprocesses, NaCl (solid) $\rightarrow Na^+$ (aq.) + Cl^- (aq.), $NaNO_3$ (solid) $\rightarrow Na^+$ (aq.) + NO_3^- (aq.), and Na (solid) + H^+ (aq.) $\rightarrow Na^+$ (aq.) + $\frac{1}{2}H_2$ (g.), a mean value of $14{\cdot}0 \pm 0{\cdot}4$ g.-cal.g.-ion^{-1}degree^{-1} has been obtained for the entropy of the Na^+ ion (relative to that of the H^+ ion) in aqueous solution at 25°C.: individual values were $14{\cdot}1 \pm 0{\cdot}5$, $14{\cdot}3 \pm 0{\cdot}5$ and $13{\cdot}7 \pm 0{\cdot}5$ respectively.[2] The U.S. Bureau of Standards selected value[1] for the entropy of the aqueous sodium ion at 25°C. is 14·4 g.-cal.g.-ion^{-1}degree^{-1}.

After using a variety of methods to calculate the effective diameter of the hydrated sodium ion, Kielland[3] took a rounded value of $4{\cdot}5 \times 10^{-8}$ cm. for this dimension and then used the Debye–Hückel theory to compute activity coefficients of the sodium ion in aqueous solution at 25°C. The resulting values are shown in Table XXII.

TABLE XXII.- ACTIVITY COEFFICIENTS OF THE Na^+ ION IN AQUEOUS SOLUTION AT 25°C.

Total Ionic Concentration	0·001	0·002	0·005	0·01	0·02	0·05	0·1	0·2
Activity Coefficient	0·975	0·964	0·947	0·928	0·902	0·86	0·82	0·775

The discrepancy between the results of various experimental methods for determining ionic solvation numbers has been discussed by Bockris[4] who, as illustration, has given the following Table for the sodium ion:-

TABLE XXIII.- THE HYDRATION NUMBER OF THE SODIUM ION AT INFINITE DILUTION BY VARIOUS EXPERIMENTAL METHODS

Method	Hydration Number
Mobility[5]	4
Water Transport[6]	3
Mobility[7]	71
Dialysis[8]	17
Partial Molar Volume[9]	1
Polarimetric (0·5 N.)[10]	700 approx.*

* Estimated from the value 1111 for NaCl.

Bockris distinguishes between primary and secondary solvation (see page 56), and the methods that he considers probably give a measure of the former - viz. those employing ionic mobility, ionic entropy, compressibility and partial molar volume - yield values of 4, 4, 4 and 1 respectively for the hydration of the sodium ion. Using a dialysis method it has been reported that three water molecules are bound to the sodium ion forming a complex aquo-metal ion, and that a further five water molecules are bound as water of hydration of the aquo-metal ion.[11] Solvation of the sodium ion in other liquids such as methyl and ethyl alcohol, acetone, acetonitrile and benzonitrile has been studied.[12,13]

Independent treatments by Latimer and co-workers[14] and by Verwey[15] have led respectively to values of 94·6 and 94·5 kg.-cal.g.-ion^{-1} for the heat of hydration of the Na^+ ion, to 89·7 and 88·5 kg.-cal.g.-ion^{-1} for the free energy of hydration, and to 17 and 19·6 g.-cal.g.-ion^{-1}degree^{-1} for the entropy of hydration. Bernal and Fowler[16] in an earlier treatment in which two different methods were used, calculated values of 114 and 116 kg.-cal.g.-ion^{-1} for the heat of hydration of the Na^+ ion. A calculation by Webb[17] of the free energy of hydration gave 99 kg.-cal.g.-ion^{-1}. Miscenko[18] using thermochemical data on the solvation of salts has given the heat of solvation of the Na^+ ion in water as 98 kg.-cal.g.-ion^{-1}, in methyl alcohol as 100 kg.-cal.g.-ion^{-1}, and in ethyl alcohol as 99 kg.-cal.g.-ion^{-1}. In separating the heats of hydration of salts into values for the individual ions Miscenko[18a] has rejected Bernal and Fowler's[16] basic assumption of approximately equal heats of hydration of the equi-radial K^+ and F^- ions, and has ascribed equal heats of hydration to the Cs^+ and I^- ions on the grounds that the difference in their radii is compensated by the dipole moment dissymmetry in the water molecule. From the Bjerrum equation for solvation the same author calculates values 169, 165 and 163 kg.-cal. g.-ion^{-1} for the heats of solvation of Na^+ in water, methyl alcohol and ethyl alcohol respectively; from the Born equation for solvation he calculates 171, 174 and 176 kg.-cal.g.-ion^{-1} for the solvation energies in the same three solvents. A number of dubious assumptions are, however, involved in these calculations.[19]

Table XXIV shows values for the equivalent conductivity or mobility of the sodium ion at infinite dilution in water. These are taken from a recent compilation[20] of ionic mobilities that uses conductivity and transport number data from several sources.

TABLE XXIV. - MOBILITY OF THE SODIUM ION AT INFINITE DILUTION IN WATER

Temp., °C.	0	5	15	18	25	35	45	55	100
λ_∞	26·5	30·3$_0$	39·7$_7$	42·8	50·10	61·5$_4$	73·7$_3$	86·8$_8$	145

The value at 100°C. is said to be reliable only within several units, while the values at 5°, 15°, 25°, 35° and 45°C. are significant to the first decimal place, and those at 0° and 18° to within two or three units in the first decimal place. In D_2O at 25°C. the mobility of the sodium ion at infinite dilution is 40·83;[21] in methyl alcohol at 25°C. it is 45·22.[22] While a considerable body of data exists for the conductivity of sodium salts in non-aqueous solvents, there is little corresponding transport data to permit calculation of precise ionic mobilities. Mobilities of the sodium ion in a variety of non-aqueous solvents have been obtained,[13,23] however, with the aid of such relationships as that between conductivity and viscosity (Walden's rule). The heat of transport[24] and entropy of transport[25] for the Na^+ ion have received attention.

Diffusion coefficients at infinite dilution may be obtained from the above mobility data using Nernst's limiting formula $D^\circ = RT\lambda_\infty/zF^2$. At 25°C. this leads to 1 33 × 10^{-5} cm.^{2}sec.$^{-1}$ for the self-diffusion coefficient of the sodium ion at infinite dilution in water. During recent years a number of studies of sodium self-diffusion have been made using radio-tracer techniques.[26-35] ^{22}Na - and sometimes ^{24}Na - has been used as the tracer isotope, and both diaphragm cell[26-28,30,34,35] and capillary tube[31-35] methods have been employed. In very dilute solutions the various methods have given fairly consistent results, but in higher concentration regions some wide differences have been observed.

A critical survey of the methods used in measuring ionic diffusion coefficients has been given by Mills and Adamson[34] who discuss also the disagreement between values obtained by the diaphragm cell and open-ended capillary methods. Higher values obtained with open-ended capillaries have been attributed in part to losses by mechanical convection. Using a new apparatus for measuring self-diffusion coefficients of Na^+ ions by means of open-ended capillaries, and by proper selection of the flow rate over the capillaries (1-3 mm./sec.), Mills[35] has obtained values over the concentration range 0·02 to 4 M. agreeing with those from diaphragm cells. These values are shown in Table XXV.

TABLE XXV.- SELF-DIFFUSION COEFFICIENTS OF $^{22}Na^+$ AT 25°C.

Na^+ conc. moles/litre	$D \times 10^5$ cm.^{2}/sec.	Na^+ conc. moles/litre	$D \times 10^5$ cm.^{2}/sec.
0·023	1·310 ± 0·005	0·981	1·251 ± 0·008
0·286	1·293 ± 0·004	2·270	1·104 ± 0·010
0·400	1·282 ± 0·008	4·373	0·905 ± 0·007
0·638	1·273 ± 0·010		

The temperature coefficient of the diffusion current of Na^+ ions at the dropping mercury electrode has been calculated by Ilkovic.[36]

Calculations of specific ionic viscosities have given a value of 0·0060 for the Na^+ ion in 0·1 N. aqueous solution.[37] Relationships between the viscosity, the mobility and the entropy of hydration of the sodium ion have been discussed.[38]

The extensive work of Okazaki on the Faraday effect in aqueous salt solutions has led to the following selection of values for the magnetorotivity of the sodium ion (in min.cm.^{2}gauss^{-1}g.-ion^{-1}), the magnetorotivity of the hydrogen ion being taken as zero:-[39]

Wave-length, A.	5900	5500	5100	4700	4300	3900	3500
$[M]$	0·17	0·17	0·21	0·27	0·36	0·48	0·60

Okazaki[40] has used $\Phi = Mnw\lambda^2/s(n^2 + 2)^2$, to define a molecular magnetorotation constant, where n and w are respectively the refractive index and Verdet's constant for light of wave-length λ, M is the molecular weight and s the density: the constant is the sum of the Φ values for the constituent ions. For the sodium ion, Φ has a value of $-0{\cdot}23 \times 10^{-14}$. Values for other ions include: Li^+, -0·68; K^+, 0·61; Rb^+, 1·51; Cs^+, 3·35; H^+, -1·41; F^-, 1·57; Cl^-, 11·17; Br^-, 19·58 (all $\times 10^{-14}$).

The refractivity of the sodium ion in aqueous solution for the sodium *D* line is 0·20.[41]

As a result of the rapid progress in the development of new ion-exchangers during recent years, a great deal of work has been carried out on the exchange of sodium ions with other ions. Exchange equilibria and exchange rates for the system Na–H[42-66] have been studied widely for a variety of cationic exchangers - in particular resins of the sulphonic acid and carboxylic acid types. Other systems to receive attention include Na–K,[67-70] Na–Ca,[71-75] Na–Ba,[42,75,78] Na–Cu,[75,79] Na–Ag,[54,68,75,80,81] Na–Tl[68,75,81] and Na–NH_4.[82,84] The adsorbability of an ion is dependent on its charge and its hydrated radius, and for the alkali metals the order of the adsorption affinities or exchange affinities is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.[42,85] Self-diffusion of the Na^+ ion and other cations has been studied in various cationic exchangers.[60,86-92] Since ion-exchange is best dealt with from the viewpoint of the exchanger rather than from that of an individual ion it will receive no detailed treatment here: several specialist books may be consulted for further information on ion-exchange and its applications.[93-96]

The Gaseous Ion

Gaseous sodium ions may be generated by the normal methods used for producing ions, for example by the use of high speed charged particles or short wave-length radiations. The emission of sodium ions on heating various sodium salts in an electric field has been studied by Poirot.[97,98] A heated filament coated with a sodium compound mixed with an iron oxide catalyst has frequently been used as a source of sodium ions.[99-101]

At 0° and 298·16°K. the U.S. Bureau of Standards selected values for the heat of formation of the gaseous sodium ion are 144·534 and 146·015 kg.-cal. g.-ion^{-1} respectively.[1]

The mobility of the Na^+ ion (in cm./sec./volt/cm.) in various gases at a pressure of 760 mm. Hg. and at 20°C. has been measured as follows:-[102,103]

Helium	23·1	Krypton	2·34
Neon	8·87	Hydrogen	13·6
Argon	3·21	Nitrogen	3·04

Later measurements in the rare gases (including xenon = 1·80 cm./sec./volt/cm.) are in close agreement with the above figures.[104] A study of the temperature variation of the mobility in helium between 92° and 477°K. has shown that the mobility increases with increase of temperature throughout this range.[105] Within 10^{-5} to 10^{-3} seconds of their liberation the mobility of Na^+ ions in hydrogen, nitrogen and helium is appreciably greater than (up to twice) that thereafter.[106-108,132] This has been attributed to the formation of ion clusters. Studies of the mobility of the Na^+ ion in all five rare gases containing small concentrations of water vapour have shown that the sodium ion acquires a cluster of water molecules which reduces its mobility by 30 to 50%.[104] In argon, krypton and xenon, an upper limit of six has been assigned to the number of water molecules in an ion cluster, but the true number is probably rather less than this. Other measurements have been made in pure water vapour.[109]

The ionization of inert gases by sodium and other alkali ions has been much studied.[101,110-119] Beeck and Mouzon[113-115] found that, in general, an inert gas is most easily ionized by the alkali metal nearest to it in the periodic classification: the potentials (ion velocities) required by Na^+ ions for them to ionize neon, argon, krypton and xenon were found to be 175, 105, 400 ± 10 and 300 ± 10 volts respectively. Later work by Varney;[101] who used a space-charge method sensitive to any resulting positive ions but unaffected by secondary electrons liberated from the walls, showed that sodium ions only produced ionization in neon (at 130 V.). It has been suggested[101] that the interference of secondary electrons may have been responsible for the results of Beeck and Mouzon. The excitation and ionization of mercury vapour by sodium ions has also been studied.[120-123] Mercury is ionized by sodium ions with energies of 88 ±4 volts.[122]

Under the influence of an electric field, sodium ions may be carried from the gas phase into a glass diaphragm.[124,125] Migration through the diaphragm occurs and ions are displaced from its cathode side. Other gaseous ions may displace sodium ions from glass diaphragms under similar conditions.[124,125] Sodium ions can also migrate through quartz plates in a direction parallel to the principal crystallographic axis of the quartz.[126,126a]

The ionic refractivity of the gaseous sodium ion for the sodium *D*-line is 0·50.[41] Values for the polarizability of the sodium ion include $0{\cdot}21 \times 10^{24}$ [127]

and 0•17 × 10^{-24}.[126] Other dielectric parameters of the sodium ions have been evaluated.[129–131]

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SOLUTIONS OF SODIUM AND SOLUBILITIES IN SODIUM

Solutions of Sodium in Liquid Ammonia

Sodium dissolves readily in liquid ammonia without reaction to give solutions that are deep blue when dilute and have a metallic, copper-like appearance when concentrated. Evaporation of the ammonia from freshly prepared solutions gives a residue of the original metal. Decomposition of the solutions is catalyzed by even minute traces of impurities. To obtain solutions of maximum stability, sodium is distilled into the preparation vessel under a vacuum of less than 10^{-3} mm. Hg., and sodium-dried ammonia is condensed on to it.[1] The vacuum system should be thoroughly outgassed, and carbon dioxide and mercury vapour should be rigorously excluded. In saturated solutions the number of ammonia molecules to each sodium atom is reported to be 5·48 at -33·8°C.[2] and 5·367 at -33·5°C.[3] Older measurements over a range of temperatures have shown that the solubility decreases slightly with rise of temperature.[4,5] Solution of sodium in liquid ammonia is an endothermic process, the heat of solution being approximately -1·4 kg.-cal./g.-atom in the neighbourhood of the boiling point of ammonia.[6,7] In the presence of dissolved salts the heat of solution is slightly different from that in the pure solvent.[7]

The rate of dissolution of sodium in liquid ammonia has been studied between -38·0° and -51·2°C.; it appears to be a diffusion-controlled process.[8] The solution rate is said to be increased by making the sodium cathodic and decreased by making it anodic.[8]

At low temperatures sodium solutions separate into two liquid phases. Kraus and Lucasse[9] examined the phase diagram down to -60°C. using the abrupt change in the electrical conductance to indicate the appearance of a second liquid phase on cooling solutions of various concentrations. The upper critical end-point of the system occurs at -41·6°C. and at a composition of 4·15 atom % of sodium. At -60°C., the two liquid phases contain 1·7 and 8·3 atom % of sodium. The phase curve differs considerably from that obtained previously by Ruff and Zedner.[10]

Dilute solutions of sodium in ammonia (~10^{-3} M.) are reported to darken noticeably and to suffer a change in the quality of the transmitted light on cooling from room temperature to -80°C.; the colour change is rapid and reversible with respect to temperature.[11] Measurements in solutions of sodium in ammonia at -60°C. have shown a single broad absorption band width with a maximum around 6800 cm.^{-1} and a half-height width of about 3000 cm.^{-1} [11a] A similar band is also shown by solutions of other metals in liquid ammonia.[11a]

A eutectic containing somewhat more than 13 atom % Na (~7 N.) is formed at -110°C.[12,13] Supercooling can, however, occur even with comparatively slow cooling. According to Birch and MacDonald[14] the solid phase consists of a non-homogeneous mixture of sodium and ammonia crystals, and a suggestion that a compound (possibly $Na(NH_3)_5$ or perhaps non-stoicheiometric) is formed[15] has been rejected. Ogg[16] has reported that rapid cooling of solutions of sodium in liquid ammonia to between -90° and -180°C. gives apparently homogeneous solid solutions. From dilute solutions the solid is blue and is visually identical with the corresponding liquid phase;[17] concentrated solutions have a bronze-like lustre.[16]

Sodium adsorbed on films of solid ammonia at -183°C. and at a pressure of 10^{-3} to 10^{-4} mm. Hg is reported to show the same colouration and optical absorption as in solutions.[18] Thin layers of ammonia containing small amounts of sodium, potassium, or lithium at 20°K. show an absorption band at about 1·15μ irrespective of the actual metal employed.[18a] There are further bands peculiar to the individual alkali metals: for sodium-ammonia layers at

TABLE XXVI. - DENSITY OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AT -33·8°C.

Moles NH_3/Atom Na	5·48 (sat.)	6·73	8·87	11·03	13·10	17·41
Density	0·5782	0·5888	0·6044	0·6163	0·6251	0·6376
Moles NH_3/Atom Na	21·07	27·26	37·84	48·04	55·17	64·14
Density	0·6494	0·6535	0·6603	0·6653	0·6681	0·6704

20°K. there is an absorption band at about 600 mμ.[18a]

The density of solutions of sodium in liquid ammonia is less than that of either of the constituents. Density values at -33·8°C. are given in Table XXVI.[2,19]

The volume expansion on solution has a maximum value of 43·14 c.c. per atom of sodium for a solution containing 11·2 moles of ammonia to each sodium atom; for a saturated solution it is 40·96 c.c. per g.-atom of sodium.[2] Other density measurements have been made for concentrations from zero up to saturation in the temperature ranges -75° to +33°C.[20] and -28° to +30°C.;[21] at 30°C. the density of a saturated solution is 0·5523.[21] Between -31·6° and -51·0°C. the density of a saturated solution varies almost linearly from 0·576 to 0·587.[22]

The coefficient of expansion decreases with increasing sodium concentration; values referred to 0°C. are:-[20]

Moles NH_3/Atom Na	5·48	6·82	11·22	21·5	69·0	103·0
$\alpha \times 10^3$	0·73	0·88	1·18	1·33	1·48	1·55

Adiabatic compressibilities of concentrated solutions of sodium in ammonia determined from sound-velocity measurements have shown a rapid increase in compressibility with increasing concentration.[22a] At 100 moles NH_3/g.atom Na the compressibility was 50×10^{-12} cm.^{2}/dyne: at 10 moles NH_3/g.atom Na it was 85×10^{-12} cm.^{2}/dyne.[22a]

Solutions of sodium in liquid ammonia have a lower viscosity than the pure solvent. Table XXVII gives viscosities in centipoises between -30° and +30°C. for sodium concentrations from zero to saturation.[23]

TABLE XXVII.- VISCOSITY (IN CENTIPOISES) OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA

g.Na/100g.NH_3	T, °C.	-30	-20	-10	0	10	20	30
0		0·247	0·217	0·194	0·174	0·157	0·144	0·132
5		0·215	0·192	0·174	0·158	0·146	0·135	0·125
10		0·176	0·162	0·150	0·140	0·132	0·125	0·118
15		0·152	0·144	0·136	0·130	0·124	0·119	0·114
20		0·144	0·137	0·132	0·127	0·122	0·119	0·115
25		0·142	0·136	0·132	0·127	0·122	0·119	0·116

Values for the vapour pressure of sodium solutions in ammonia at -33°C. are shown in Table XXVIII.[2]

TABLE XXVIII. - VAPOUR PRESSURE OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AT -33°C.

Moles NH_3/Atom Na	2·839	3·995	4·532	5·461	6·008	6·469
Pressure, mm. Hg.	397·0	397·0	401·0	403·0	486·0	544·5
Moles NH_3/Atom Na	6·910	7·314	8·367	9·521	10·745	13·561
Pressure, mm. Hg.	592·5	625·0	681·5	732·2	745·5	767·0

TABLE XXIX.- EQUIVALENT CONDUCTIVITY OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AT -33·5°C.

V	0·1081	0·1804	0·2768	0·5047	0·7861	1·038	6·305
Λ	545,600	484,700	296,200	82,490	12,350	3,228	554·7
V	13·86	30·40	65·60	318·6	3,479	17,260	37,880
Λ	478·3	478·5	540·3	773·4	988·6	1016·0	1034·0

A saturated solution boils at -0·2°C.[10]

The electrical conductivity of dilute solutions of sodium in ammonia varies in the same way as that of ordinary electrolytes, the equivalent conductivity approaching a limiting value at infinite dilution.[24] Working at -33·5°C., Kraus[24] found a minimum equivalent conductivity (~475) at a concentration of approximately 0·05 N.; thereafter the equivalent conductivity rose rapidly with increasing concentration. For the selection of values[3,24,25] given in Table XXIX. the 'dilutions', V, represent the number of litres of pure ammonia in which one gram atom of sodium is dissolved; the equivalent conductivity, Λ, is given as $1000\,V \times$ specific conductivity.

Other conductivity measurements by Gibson and Phipps[26] are in general agreement with those of Kraus. Measurements at -33·5°, -48·5° and -70·0°C. showed, in each case, a minimum equivalent conductivity at a concentration of about 0·04 N. At these three temperatures the minimum equivalent conductivity values were 460, 360 and 235 respectively[24] (dilutions in litres of solution per g. atom Na). A saturated solution of sodium in ammonia at -33·5°C. has a specific conductance of $0{\cdot}5047 \times 10^4$ ohms^{-1}cm.$^{-1}$ which is approximately half the specific conductance of mercury at 0°C.; the atomic conductance of the saturated solution is $0{\cdot}672 \times 10^6$ reciprocal ohms.[3] In these concentrated solutions the conduction is metallic in character, and ammonia solutions of the alkali metals have been regarded as forming a link between electrolytic and metallic conductors.[24] (See below).

The temperature coefficient of conductance, $d\kappa/dT$, increases with increase of temperature.[26,27] Gibson and Phipps[26] found that the logarithmic coefficient $d \ln \kappa/dT$ had a value independent of temperature, *i.e.* the conductivity is an exponential function of temperature. At dilutions in the vicinity of 100 litres this logarithmic coefficient had a value of about 0·02. Kraus and Lucasse[28] have shown that the temperature coefficient is much greater in dilute solutions than in concentrated solutions. Near the saturation point they found a temperature coefficient of ~0·066% per degree; the coefficient increased to a maximum value of ~3·6% per degree at a dilution of 1·1 litre and thereafter decreased to 1·55% per degree at dilutions above 4 litres. A value of 2·25% per degree has been reported in more dilute solutions.[24]

In dilute ammonia solutions the conductivities of sodium and potassium, and of sodium and lithium,, are practically additive, there being no evidence of compound formation between the metals.[29] Conductivity measurements have also been made on mixtures of sodium metal and sodium salts in liquid ammonia.[30] A study of the Wien effect in solutions of alkali metals in ammonia at -78°C. has shown that a 4% increase in conductivity occurs on applying an electrical field of about 15kv./cm.[30a]

According to Kraus,[24,25] sodium atoms, sodium ions, free electrons and solvated electrons are present in equilibrium in ammonia solutions of sodium:-

$$\mathrm{Na} \rightleftharpoons \mathrm{Na}^+ + e^-$$
$$e^- + n\mathrm{NH}_3 \rightleftharpoons e^-(\mathrm{NH}_3)_n$$

In dilute solutions the electrons arising from the ionization of the sodium are solvated, and the decreasing degree of ionization with increasing sodium concentration results in a corresponding fall in the equivalent conductance. In more concentrated solutions some of the electrons become free from associated ammonia molecules, and the increased mobility of the negative carriers is made manifest by an increase in the conductance. At high sodium concentrations, the free electrons are responsible for the characteristic 'metallic' conduction. While this theory gives a satisfactory explanation of many facts, including the conductance behaviour, it meets difficulties when some other properties, - in particular, magnetic susceptibility - are considered.[31] Farkas[32] has given a quantum mechanical treatment of the electrical conduction in ammonia silutions of alkali metals in which it is assumed that the electrons are restrictedly free at all concentrations, and that conduction occurs by electrons undergoing 'non-mechanical' transitions from atom to atom in the direction of the field, the distance between the ordered array of atoms varying with the concentration. The theory leads to results in moderately good agreement with experiment for solutions containing one to five moles of sodium per litre of solution. More recently it has been proposed that the electrons are trapped in the solvent, these existing in the liquid cavities which serve to trap electrons either singly or in pairs.[32a,32b,61] This model which is compatible with a large body of experimental data has been discussed and elaborated by several authors.[11a,32c-32g]

Chittum and Hunt[33] have criticized the solvated electron theory and have maintained that alkali metals are dispersed in liquid ammonia as colloidal particles. In support of their theory they report that dilute solutions of sodium in ammonia display a Tyndall cone and that the blue colour of a sodium solution in ammonia cannot be made to pass through a membrane by electrodialysis. As a result of experiments with an ultramicroscope and an ultrafilter, Kruger[34] has also concluded that sodium-ammonia solutions are colloidal. Filtration removed the sodium and its associated blue colour, and resulted in a large increase in the electrical resistance of the solution. Other workers have criticized the method of preparation of the above 'colloidal' solutions, and deny that solutions of sodium in ammonia are colloidal in nature.[31,35]

Between 1945 and 1950 the question of superconductivity in solid sodium-ammonia solutions received considerable attention. But now that all the evidence can be examined, by far the greater part of it seems to point to the absence of such superconductivity in these solutions. Ogg[17] in 1945 observed a marked positive temperature coefficient of resistance in dilute solidified solutions (10^{-4} to 10^{-2}M) of sodium in ammonia at -80° to -100°C. in contrast to the negative coefficient for liquid solutions. Extremely rapid freezing of approximately molar solutions from -33° to -95°C. reduced the resistance by a factor of over 600.[16] Solid ring samples of sodium-ammonia, prepared by rapid freezing in a magnetic field, were found by Ogg to possess a magnetic moment which was taken to be indicative of a persistent current.[16] This report of superconductivity in sodium solutions at liquid air temperatures aroused considerable interest and led to much further investigation since all other known cases of superconductivity occur below about 10° to 14°K.[36,37] Other workers who have looked for persistent currents in ring samples or have made direct resistivity measurements have not, however, confirmed the existence of superconductivity in these solutions.[38-47] Ogg[48] in reply to such reports has considered that the solid cracks into a micro-mosaic pattern, and that it is a rare accident when the residual contact resistances are sufficiently small to allow an appreciable persistent current. He states that out of about 200 experiments performed by him only 7 gave a positive result. Several other workers have, however, carried out a considerable number of experiments with frozen rings with no positive results.[38,39,44,45] Hodgins[49] did observe small persistent currents - though much less pronounced than found by Ogg - in 4 out of 115 experiments carried out with frozen rings, but in a later paper[50] in which he confirms his earlier observations of minute persistent currents, it is thought unlikely that these currents are due to superconductivity since their direction did not change with the direction of the magnetic field. MacDonald *et al.*[41] in their first experiments observed transient magnetic moments of the order of magnitude described by Hodgins, but these were traced to iron objects in the laboratory or to very small vibrations in the search coil: 85 experiments under more stringent conditions gave no positive results. Other studies have shown that there is a finite resistance in solid sodium-ammonia solutions at low temperatures,[47] and that the residual resistance is due to the solution itself and not to contact resistance.[38,46] At −183°C. the specific resistance of a saturated solution has been given as 5×10^{-4} ohm cm. compared with 2×10^{-4} ohm cm. at −33·5°C.[47] It has been demonstrated that the sharp decrease of resistance occurs just at the solidification point,[44] and that it occurs with slow as well as with rapid cooling;[46] the large change in resistivity has been attributed to the formation upon cooling of a bronze-coloured, sodium-rich phase.[46] A study has been made of the effect of rapid and slow freezing on the resistivity of a 2·1% solution of sodium in ammonia from −100° to −160°C.; with rapid freezing there is a maximum resistance at −114°C.[41] Suggestions have been advanced to account for the anomalies observed by Ogg other than by supposing the solid to be superconducting.[38,43]

The thermoelectric properties of solutions of sodium in liquid ammonia at −33°C. have been studied over the concentration range 0·002 **M.** to saturation.[1] The thermoelectric power increases with decreasing concentration over the whole range; in concentrated solutions its value is of the order of magnitude characteristic of typical metals.

In concentrated solutions sodium exhibits a weak paramagnetism; in dilute solutions it is strongly paramagnetic.[20,51] At intermediate concentrations (moles NH_3/Na = 50 to 100) the atomic susceptibility (χ_A) passes through a minimum, and at lower temperatures it in fact becomes negative.[20] Thus, for an ammonia/sodium molecular ratio of 100 the atomic susceptibility at −60°C. is -28×10^{-6} and at −35°C. it is $+27 \times 10^{-6}$.[20] Figure 5 shows a plot of $\chi_A \times T$ against the logarithm of the molecular ratio NH_3/Na at −75°C. and at −35°C.[20] To explain these results, Huster[20] has assumed the existence of Na_2 molecules and the equilibrium:-

$$Na_2 \rightleftharpoons 2Na^+ + 2e^-$$

Freed and Thode[52] found that at 230°K. in 0·5 N. solution the atomic susceptibility was equal to that in the bulk metal; in 0·017 N. solution the atomic susceptibility exceeded that of the bulk metal by a factor of about 30 while in 0·0022 N. solution the factor was about 100. For very dilute solutions the susceptibility corresponds to a magnetic moment of 1 Bohr magneton per atom.[51] At −35° and −75°C. the volume susceptibility of solutions of sodium in ammonia has a substantially constant value ($\sim -0{\cdot}7 \times 10^{-6}$) independent of sodium concentration between 10^{-4} and 1 N.; at higher concentrations it falls rapidly.[20] Other measurements at 78° and 195°K. show a similar behaviour.[42] Prior to any of the above magnetic studies, a paramagnetism associated with sodium dissolved in ammonia had been observed by Taylor.[53]

Paramagnetic resonance absorption has been observed in ammonia solutions of sodium at low field strengths, and the signal amplitude has been found to be sensitive to the sodium concentration.[54,55,32f] The line width is very small, values as low as 0·02 gauss being recorded at the points of maximum slope.[32f] Resonance experiments performed at a frequency of 49 Mc./sec. in a precession field of 17·5 gauss and using a 0·1 M. sodium solution have shown an increase of signal amplitude with increasing temperature.[55]

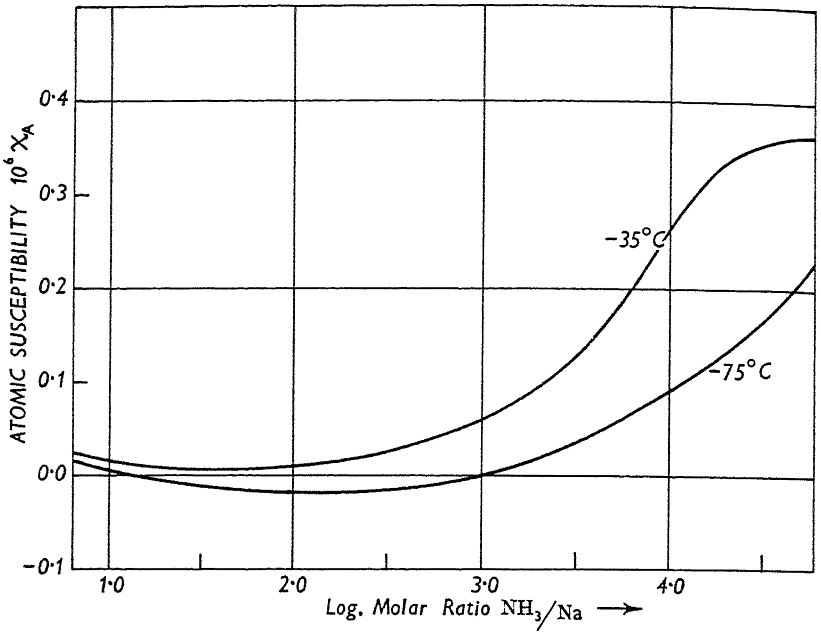

FIG. 5.- MAGNETIC SUSCEPTIBILITY OF SODIUM DISSOLVED IN AMMONIA

At lower sodium concentrations (0·001M.) the effect was less marked.

A 0·033 M. solution of sodium in ammonia at -53°C. gave a half life of 37 seconds for the para-/ortho-hydrogen conversion.[56]

Solutions of sodium in liquid ammonia show photoelectric emission,[57-59] but there is no observable photovoltaic effect in the system.[60] The long-wave threshold for photoelectric emission changes from 7,700 A. for saturated solutions to about 15,000 A. for 0·0001 to 0·00001 M. sodium solutions.[58] For concentrated solutions, the spectral distribution of the quantum yield is similar to that for the solid metal.[57] At -78°C., concentrated solutions give a maximum response at 5,200 A.[59] For dilute solutions, the maximum sensitivity is in the near infra-red.[58] A marked increase in the electrical conductivity of very dilute solutions (10^{-5}M.) in the temperature range -35° to -75°C. has been observed upon irradiating with visible light.[61]

The solubility curve for mixtures of sodium and potassium in ammonia shows three branches corresponding to the solubility of pure sodium, the compound Na_2K, and pure potassium.[29] For mixtures of sodium and lithium, the curve is linear from pure sodium to pure lithium.[29] A study of the system Na-NaI-NH_3 at -33° to -31°C. has shown that dilute solutions of sodium in ammonia are miscible with salt solutions, but that concentrated solutions are not.[62]

Several reviews of the properties and constitution of metal-ammonia solutions have appeared.[37,63-65]

Decomposition of sodium-ammonia solutions and reactions of sodium dissolved in ammonia are discussed under 'Chemical Properties'.

Solutions of Sodium in its Salts

Sodium dissolves readily in fused sodium chloride, as little as 0·1% im-

TABLE XXX. - SOLUBILITY OF SODIUM IN SODIUM HALIDES

NaF		NaCl		NaBr		NaI	
T, °C.	Mole % Na	*T*, °C.	Mole % Na	*T*, °C.	Mole % Na	*T*, °C.	Mole % Na
979	0·19*	750	0·08*	650	0·04*	674	3·2
983	0·96*	790	0·15*	685	0·07*	722	4·1
1000	7·6	810	2·8	720	0·15	763	6·2
1001	15·8	826	4·9	750	4·6	810	8·3
1015	14·8	890	10·2	799	6·8	849	9·9
		929	21·3	852	7·3	909	14·9
		950	25·1	909	12·2	954	20·8
		976	32·0	950	~15·0		
		1001	33·0				

parting a deep red colour to the melt.[66] Higher concentrations of sodium give dark red to reddish-brown solutions. Slow crystallization of these solutions yields a blue product which dissolves in water with evolution of hydrogen. Lorenz and Winzer[66] gave the solubility in sodium chloride as 4·2% by weight at 800°C., and 15–20% at 850°C. These workers also made solubility measurements in sodium chloride–calcium chloride mixtures between 500° and 800°C. A recent study of the four binary sodium/sodium halide systems has given information concerning their phase diagrams at both high salt and high sodium concentrations.[67] From the trends in the portions of the curves studied it appeared that sodium would be completely miscible with each of its halides at temperatures above about 1000° to 1100°C. Table XXX gives a selection of the figures for the solubility of sodium in its halides; asterisked values are solubilities in the solid salt phase. In subsequent work[67a] the consolute temperatures and consolute mole fractions of sodium for each of the sodium/sodium halide systems were found to be as follows:

	Na/NaF	Na/NaCl	Na/NaBr	Na/NaI
Consolute Temperature, °C.	1182	1080	1025	1033
Consolute Mole Fraction Na	0·28	0·50	0·52	0·50

In each of the systems the dissolved sodium lowers the melting point of the pure salt by several degrees, and the eutectic temperatures and compositions are as follows:-

	NaF	NaCl	NaBr	NaI
m.p. of pure salt, °C. ± 0·5	995	803	747	661
Na/salt eutectic, °C.	990	794	740	656
Mole % Na in solid salt	~1	~0·2	~0·3	—
Mole % Na in liquid salt	~2	2·4	4·2	2·9
Mole % salt in liquid metal	17·0	2·3	3·4	1·4

Earlier electromotive force measurements in the system Na/NaBr indicated a much lower value of less than 1 mole % for the solubility of sodium in sodium bromide at about 850°C.[68] Table XXXI gives values for the solubility of sodium halides in liquid sodium: in the case of the asterisked figures the phase in equilibrium with the liquid metal is solid salt.[67]

From the temperature coefficients of solubility, the partial molar heats of solution of the solid salts in liquid sodium are: sodium fluoride, 26 ± 2 kg.-cal.; sodium chloride, 20 ± 3 kg.-cal.; sodium bromide, 24 ± 1 kg.-cal.; sodium iodide, 28 ± 2 kg.-cal. There is no evidence for the existence of solid compounds such as Na_2X in these systems.[67]

TABLE XXXI.- SOLUBILITY OF SODIUM HALIDES IN LIQUID SODIUM

NaF		NaCl		NaBr		NaI	
T, °C.	Mole % salt	*T*, °C.	Mole % salt	*T*, °C.	Mole % salt	*T*, °C.	Mole % salt
801	2·4*	550	0·12*	550	0·21*	550	0·06*
849	5·3*	649	0·75*	600	0·41*	584	0·28*
900	8·1*	750	1·8*	660	1·1*	608	0·60*
952	10·7*	790	2·9*	721	2·4*	652	1·2*
983	16·4*	832	4·2	757	3·3	699	1·5
1004	17·3	874	5·8	825	4·6	800	2·8
1048	20·0	913	8·3	894	7·8	882	5·7
1078	23·6	957	11·1	955	12·1	959	10·5

Electrical conductivity measurements have been made in the systems sodium/sodium chloride and sodium/sodium bromide.[68a] Specific conductance increases continuously with metal concentration but equivalent conductance shows a more complex concentration dependence.

Additive colouration of alkali halide crystals by contact with liquid sodium or sodium vapour is discussed on page 389.

Early work[69] gave figures for the solubility of sodium in fused sodium hydroxide, and regarded it as a case of simple solution; but it has since been shown that chemical change may occur in this system.[70-72] A blue colour has been reported for solutions of sodium in caustic soda.[73]

Other Solutions of Sodium

Moissan[74] in 1899 reported that sodium dissolves in methylamine, and other later workers[26,75] have also reported a slight or moderate solubility. Recent work has shown, however, that purified methylamine, practically free from water and ammonia, dissolves sodium at temperatures below 0°C. only after several hours, to give a solution of low sodium concentration.[76] The slight solubility is attributable to residual contamination by ammonia.[76] The absorption spectrum of the blue solutions in methylamine has been studied,[11a,75,76] as has that in ammonia/methylamine and ammonia/ethylamine mixtures.[11a] Sodium is reported to be soluble in ethylenediamine,[65] but it is insoluble in ethylamine[77,78] and in secondary and tertiary amines.[77]

Solubilities in Sodium

The use of liquid sodium as a heat transfer agent has led to work on the solubility of a number of impurities in the metal. Oxygen-containing impurities are of considerable practical importance since the presence of oxygen results in increased corrosion of containers, and the corrosion products adversely affect heat transfer coefficients. Also precipitation of sodium oxide in the cooler parts of the system can produce blockages. Values for the solubility of sodium monoxide in sodium tend to be rather variable: Fig. 6 shows results obtained in three American laboratories.[79,80]

Sodium hydroxide is soluble in liquid sodium to the extent of $\sim$0·02% at 350°C.[79,80] The solubilities of sodium hydride and sodium carbonate in liquid sodium are given in Tables XXXII and XXXIII.[81] The presence of these two impurities can lead to errors in the analysis for oxygen in sodium by the amalgamation method.[81]

Barium oxide has a solubility of less than 0·05 wt.% in sodium at 500°C.[82]

Figures for the solubility of sodium halides in the metal at temperatures greater than 550°C. have been given above (Table XXXI). At 400°C. the solubility of sodium chloride in liquid sodium is reported to be considerably

24·3

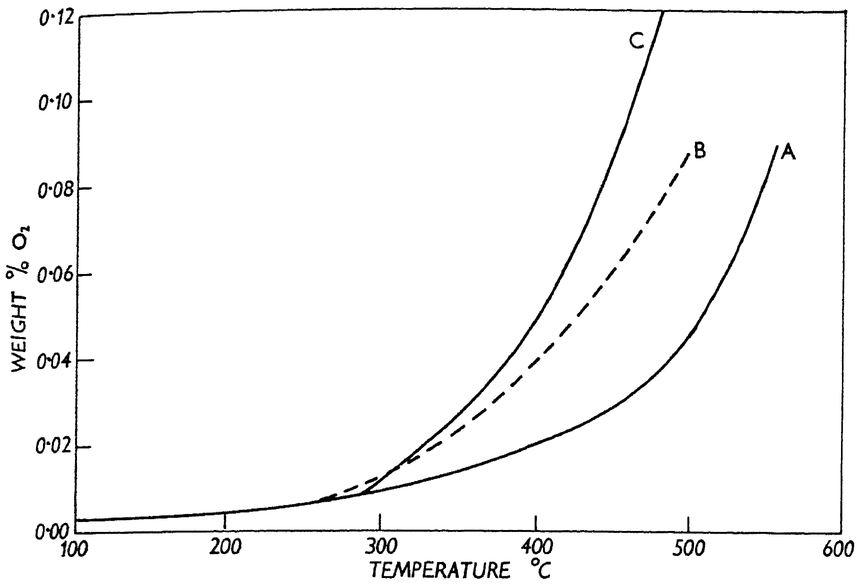

FIG. 6.- SOLUBILITY OF SODIUM MONOXIDE IN SODIUM
A. Naval Research Laboratory data
B. Knolls Atomic Power Laboratory data
C. Mine Safety Appliances Co. data.

TABLE XXXII.- SOLUBILITY OF SODIUM HYDRIDE IN LIQUID SODIUM

Temperature (°C.)	NaH (Wt.%)
250	0·005
300	0·040
350	0·300
400	1·45
445	4·29

TABLE XXXIII.- SOLUBILITY OF SODIUM CARBONATE IN LIQUID SODIUM

Temperature (°C.)	Na_2CO_3 (Wt.%)
150	0·002
200	0·005
300	0·016
385	0·027

less than 9 p.p.m. and probably less than 1 p.p.m.[81]

Reciprocal solubilities of other metals in sodium are dealt with under 'Sodium Alloys' (see pages 548-621).

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ATOMIC WEIGHT AND ISOTOPES

Until 1953 the value for the atomic weight of sodium accepted by the International Commission on Atomic Weights had for many years remained at 22·997, a value that derived from determinations of the sodium chloride : silver, and sodium chloride : silver chloride ratios by Richards and Wells[1] in 1905. An accumulation of evidence, mainly from mass spectrometric measurements and nuclear calculations (see page 438), indicated that this value was too high and finally led to the adoption in 1953 of the lower value 22·991.[2]

For elements such as sodium that have no natural isotopes (see page 438), the accuracy and relative ease associated with determinations of the masses of single nuclear species by physical methods (mass spectrometry and nuclear energy calculations) have now resulted in these more recent methods completely displacing chemical methods for the determination of atomic weight. A few chemical determinations of the atomic weight of sodium have, however, been made during the last thirty years or so.[3-5]

Johnson,[4] in 1933, prepared pure sodium chloride by precipitating the salt by means of hydrogen chloride from a saturated solution and then crystallizing it from water: each stage was carried out three times. A weighed quantity of

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the fused salt was dissolved in water and used to precipitate silver chloride from an approximately equivalent amount of silver nitrate solution prepared from a weighed quantity of pure silver. After standing for some time, a portion of the supernatant liquid was withdrawn, filtered and analysed nephelometrically or potentiometrically for excess silver or chloride. Preliminary analyses enabled the silver and chloride contents of the solutions to be adjusted more closely to exact equivalence either by modifying the starting amounts of sodium chloride and silver or by making additions of dilute standard silver nitrate or sodium chloride solution. The end point was usually determined by a number of sets of analyses over a period of several days. In other experiments the precipitated silver chloride was collected quantitatively. Taking Cl = 35·457 and Ag = 107·880 (still their accepted values), the atomic weight of sodium obtained from both sets of experiments was 22·994.

In 1934 Baxter and Hale[5] obtained a value of 3·14950 for the ratio I_2O_5 : Na_2CO_3. They used carefully purified iodine pentoxide and sodium carbonate, and the end point for the reaction between these substances was determined with bromothymol-blue after carbon dioxide had been expelled. Uncertainties at that time in the atomic weights of carbon and iodine prevented calculation of an unequivocal atomic weight for sodium. When 1953 values are taken for carbon and iodine the above ratio gives 22·991 for the atomic weight of sodium.

Earlier values for the Na_2CO_3 : 2Ag[6] Na_2CO_3 : 2AgBr[6] Na_2CO_3 : Na_2SO_4[6] and Na_2CO_3 : I_2O_5[5] ratios, reconsidered in the light of a then new value (12·010)[7] for the atomic weight of carbon, led Scott and Hurley[8] to suggest in 1937 that the value of 22·997 for the atomic weight of sodium was 0·003 to 0·004 units too high.

From density and *X*-ray data for solid sodium chloride, values of 22·980,[9] 22·996[10,10a] and 22·997[11] have been reported for the atomic mass of sodium.

In his classical work with the mass spectrograph, Aston[12,13] showed that sodium was a simple element with but one isotope of mass number 23. Later work by Bainbridge[14] showed that if ^{21}Na, ^{22}Na or ^{25}Na exists it does so to the extent of less than one part in 3000, 800 and 3000 respectively of ^{23}Na. In 1936, mass spectrographic evidence[15] was reported for the existence of ^{22}Na with a ^{23}Na/^{22}Na ratio of 5000 ± 500, while the upper limits for ^{20}Na, ^{21}Na, ^{24}Na and ^{25}Na were set at 1 part in 50,000 of ^{23}Na. A later careful search for ^{22}Na has not, however, confirmed the natural existence of this isotope and the upper limit for its abundance has been given as 1 part in 30,000 of ^{23}Na.[16]

Several sodium isotopes with short half lives have been produced artificially by nuclear reactions. A recent review which also summarizes methods of production and disintegration schemes lists the following:[17]

Isotope	Approx. Half Life
^{20}Na	0·3 sec.
^{21}Na	23 sec.
^{22}Na	2·7 yrs.
^{24}Na	15 hours
^{25}Na	60 sec.

Mass spectrometric measurements[18] have given a value of 22·99665 ± 0·00008 for the mass of ^{23}Na. This and the following atomic masses are all on the physical scale (^{16}O = 16). From the energies of a series of three reactions by which ^{23}Na is converted into ^{16}O, Way[19] calculated a value of 22·9971 for the mass of the ^{23}Na atom. By combining two reactions starting with ^{22}Ne he obtained ^{23}Na = 22·9972, and a series of three steps from aluminium to sodium gave ^{23}Na = 22·9968. Other values for the mass of ^{23}Na derived from nuclear reaction energies are 22·997055 ± 0·000025[20] and

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22·9972.[21] The above six physical determinations lead to an average value of 22·9970 for the mass of ^{23}Na. Since sodium is a simple element this value can be converted directly to the chemical scale to give the atomic weight of sodium. Such conversion (factor = 1·000275) yields an atomic weight of 22·9907. As discussed above (see page 437), this value provides the main basis for the adoption of Na = 22·991 as the International Atomic Weight.

Masses obtained from nuclear calculations for artificial sodium isotopes[20] include ^{21}Na = 21·004286 ± 0·000039, ^{22}Na = 22·001409 ± 0·000025 and ^{24}Na = 23·998568 ± 0·000026, all on the physical scale.

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SECTION XXV

THE CHEMICAL PROPERTIES OF SODIUM

By (MRS.) F. DICKINSON

A freshly cut surface of sodium, viewed in the dark, emits a greenish light, the intensity of which increases as the temperature is raised. The chemiluminescence consists of a narrow band with a maximum at about 5000A. believed to be due to the rupture of the hydrogen-oxygen bond in water vapour, resulting in the formation of sodium hydroxide.[1-3] An electron diffraction study of the surface of sodium after exposure for five minutes to air or air containing water vapour has shown that in the first case sodium hydroxide crystals of grain size 10^3A. are arranged at random on the metal surface, and in the second case larger, oriented sodium hydroxide crystals are present.[4] Carbon dioxide in the air converts some of the hydroxide to sodium bicarbonate.[5-7]

Liquid sodium ignites in air at about 125°C. and burns quietly in a comparatively dry atmosphere giving off dense, white, caustic smoke. The temperature of the burning mass increases rapidly to 833°-889°C. In this condition it spalls concrete, consumes asbestos, fire-brick and similar materials and reacts with glass. It also reacts violently with common fire extinguishers such as water, carbon dioxide snow and carbon tetrachloride.

Liquid sodium fires can be safely extinguished with dry sodium carbonate, and blanketed with nitrogen.[8,9]

Dry oxygen forms a grey coating on a freshly cut surface of sodium and the reaction quickly ceases if moisture is not present to remove the protective film. Whereas some workers have stated that the reaction is accompanied by luminescence[10] others have found that no luminescence occurs if the oxygen is freed from moisture.[2,3] The rate of oxidation at a surface of sodium at room temperature depends markedly on the presence of a small amount of inert gas. With pure oxygen the rate is very low and a white layer of sodium monoxide is formed. With a small amount of nitrogen the rate is very high and coloured films of oxide are formed. If the oxygen pressure is raised the rate is suddenly lowered; heating to about 90° C. results in a fast reaction rate.[11]

More recently the oxidation rate of sodium at −79°, −20°, 25°, 35° and 48°C. has been studied by Cathcart, Hall and Smith. In dry oxygen the rate is found to be small and the oxide film highly protective. A slight increase in the rate of oxidation which occurs at 48°C. after 25,000 to 30,000 minutes has not been explained.[12]

An early literature reference states that sodium can be distilled in very dry oxygen.[13]

The production of sodium monoxide is brought about by treating sodium amalgam with oxygen; a mixture of sodium monoxide and peroxide is first formed and the peroxide is then reduced by sodium amalgam to the monoxide.[14]

When about 0·5g. of sodium is heated gently in a porcelain dish, it melts and spreads owing to the lowering of its surface tension; the metal is coated with a blue skin, which phosphoresces in the dark, and on cautious treatment with water the reaction product gives off oxygen. Treatment with dilute sulphuric acid yields hydrogen peroxide which turns starch-iodide paper blue. These simple experiments demonstrate the ease with which sodium is converted to sodium peroxide.[15]

Sodium peroxide may be formed in two stages: oxidation of the metal in dry air to form the monoxide, followed by oxidation with 90% oxygen to yield sodium peroxide.[16] Sodium peroxide is also formed by the rapid oxidation of sodium in liquid ammonia, see page 509.

The rate of oxidation of sodium may be controlled by allowing a mixture of the metal and an inert material, such as 10% of sodium and 90% of sodium monoxide, both in finely divided form, to react with oxygen to form additional sodium monoxide or peroxide, more sodium being added as required.[17]

A superficial layer of sodium monoxide on particles of sodium peroxide is obtained by mixing together sodium and sodium peroxide in an inert atmosphere at a temperature above the melting point of sodium but below the reaction temperature, in order to form a film of sodium on the peroxide particles, and then raising the temperature to that required for the reaction.[18]

The production of sodium monoxide and peroxide from molten sodium and sodium peroxide, and arrangements for continuous operation, have been described.[19-21] In the manufacture of alkali peroxides the molten alkali metals are atomized in spray guns. An oxidizing atmosphere is used to cause the formation of peroxides. The peroxide is cooled quickly by the flow of air so that the temperature is reduced below the fusion temperature of the oxide. A considerable excess of air is necessary, and since sodium is less reactive than potassium, the former must be atomized to a more minute degree.[22,23] Sodium amalgams on exposure to air are not peroxidized as observed by Rinck *et al.*,[24] even at 60°C. and with a larger contact area. When, however, 0·035-0·50 mole fraction of potassium is added to the sodium and amalgamated, potassium superoxide, which is readily formed, catalyzes the formation of sodium peroxide. No oxidation of mercury to the oxide Hg_2O occurs as is found in the peroxidation of potassium amalgams in the absence of sodium.[25] According to Feldmann,[26] sodium amalgam containing 0·264% of sodium reacts with oxygen at 10 atm. pressure at room temperature to give a quantitative yield of sodium peroxide, but when the reaction mixture is allowed to stand, all of the peroxide ultimately disappears and the mercury is oxidized. If the reaction is carried out at 100°C. the oxide HgO is immediately formed and only a trace of sodium peroxide is produced. In this case sodium acts as a catalyst because mercury is not oxidized under these conditions in the absence of sodium. If sodium amalgam is agitated with oxygen at room temperature, the amalgam becomes pasty owing to the formation of sodium peroxide, but the reaction is inhibited by the presence of water. Decomposition with sulphuric acid of sodium peroxide formed by the oxidation of sodium amalgam does not give a good yield of hydrogen peroxide and with 20% sulphuric acid at −1°C. a concentration of only 0·5% hydrogen peroxide is obtained. Lower temperatures and other acids such as phosphoric acid are no better. It is also difficult to separate sodium peroxide from mercury either by centrifuging or by distillation under reduced pressure. When a 0·1% sodium amalgam is vigorously agitated with oxygen so that the amalgam surface is continuously destroyed, a 98·7% yield of sodium peroxide is obtained in 41 minutes at 20°C. The product is filtered on a glass suction filter.[27] The peroxide undergoes a secondary reaction on standing, giving varying amounts of sodium monoxide.[28]

Examples are given in a patent specification for the production of sodium peroxide and other compounds by treating sodium amalgam with a gaseous reactant, oxygen in the case of sodium peroxide, under water-free conditions.[29]

The production of sodium peroxide from sodium amalgam and the economic aspect of the production of sodium peroxide by the process described above have been reviewed by Nicolai.[30] When this process is carried out in the presence of water, hydrogen peroxide is formed: $2Na + O_2 + 2H_2O \rightarrow H_2O_2 + 2NaOH$.

Sodium superoxide, NaO_2, is prepared by heating metallic sodium at 300°C. with oxygen at a pressure of 2700 lb. per sq. in. The product obtained evolves oxygen on contact with moisture equivalent to a 70% conversion to sodium superoxide. The best conversions are obtained when sodium peroxide, of low bulk density and a high surface area, prepared by the atomization of molten metallic sodium according to the patent specification,[23] is heated in a bomb at a temperature of at least 200°C. in contact with oxygen at a pressure of at least 1500 lb. per sq. in. A product of low available oxygen content results if the peroxide is dense or in the form of hard granules.[31]

Sodium superoxide, NaO_2, and sodium peroxide, Na_2O_2 are reduced by molten sodium at 500°C. to sodium monoxide, Na_2O.[32]

Sodium superoxide is formed by the rapid oxidation of sodium in liquid ammonia at -77°C. (see page 509).

The following values are given for the heat of formation of sodium monoxide, expressed as kg.-cal./g.mole:-

$$2Na(c) + 0{\cdot}5O_2(g) \rightarrow Na_2O(c), \Delta H^\circ_{298} = -100{\cdot}7;^{33}$$
$$-99{\cdot}4;^{34}\ \Delta H^\circ_{293} = -102{\cdot}87 \pm 0{\cdot}32.^{35}$$

The free energy expressed as kg.-cal./g.mole is given as, $\Delta F^\circ_{298} = -91{\cdot}4;$[33] $-90{\cdot}0$.[34] Under the following conditions:-

$$2Na(l) + 0{\cdot}5O_2(g) \rightarrow Na_2O(c), \Delta H^\circ_{400} = -104{\cdot}20$$

and $\Delta H^\circ_{500} = -104{\cdot}21$.[33]

For sodium peroxide: $2Na(c) + O_2(g) \rightarrow Na_2O_2(c), \Delta H^\circ_{298} = -120{\cdot}6$,[33 34] and at about 20°C., $\Delta H^\circ = -124{\cdot}84 \pm 0{\cdot}32$.[35]

Gilles and Margrave give a value of $-122{\cdot}1 \pm 1{\cdot}2$ kg.-cal./g.mole for the heat of formation of sodium peroxide at 298°K.[36]

For the heat of formation of sodium superoxide:-

$$Na(c) + O_2(g) \rightarrow NaO_2(c), \Delta H^\circ_{298} = -61{\cdot}9 \text{ kg.-cal./g.mole}^{33,34}$$

Gilles and Margrave give $-62{\cdot}1 \pm 0{\cdot}7$ kg.-cal./g.mole for the heat of formation of sodium superoxide at 298°K.[36]

It is unlikely that sodium peroxide or superoxide is stable in the presence of liquid sodium.[33]

Haber and Zisch have observed the formation of a small cone-shaped flame when nitrogen, laden with sodium vapour at atmospheric pressure and at a temperature below which black-body radiation would be visible, *i.e.* below 525°C., enters a space containing oxygen.[37]

The reaction of sodium vapour with oxygen has been studied kinetically by the method developed by Hartel and Polanyi[38] for the determination of rates of slow atomic reactions. Sodium vapour at an initial pressure (pNa) is introduced with an inert gas through a nozzle where it comes in contact with oxygen. The distance to which the sodium vapour penetrates is determined by means of a sodium resonance lamp. Surface reactions are minimized by introducing the reactants in an inert gas stream, the rate of diffusion of sodium in nitrogen being such that the sodium vapour leaving the nozzle is used up before it reaches the walls of the vessel. This largely avoids the difficulties involved when a solid deposit is formed. The procedure is described as the 'diffusion flame' method because the reaction is also accompanied by a luminescence. If pNa and po are the pressures of sodium at the centre and edge of the flame respectively, R the radius of the flame, and r that of the nozzle, δ the diffusion coefficient of sodium in nitrogen, px the pressure of oxygen in the reaction vessel and T the absolute temperature, then the velocity constant for the reaction is given by:-

$$k = \frac{(\ln p\mathrm{Na}/po - \ln R/r)^2}{(R - r)^2} \cdot \frac{\delta}{px} \cdot \frac{1}{T}$$

Under the conditions of their experiments, using sodium vapour at 0·0016mm. pressure, argon, helium or nitrogen at 2–10mm., oxygen at 0·02–0·38mm. and a reaction temperature of 250°C., Haber and Sachsse[39] have found that the reaction velocity constant varies almost linearly with the pressure of the inert carrier gas. A termolecular reaction occurs: $Na + O_2 + X \rightarrow NaO_2 + X$ (where X = He, A or N_2), the inert gas acting as a 'third' body, and carrying away the energy of the reaction, followed by: $NaO_2 + Na \rightarrow 2NaO$, finally giving a deposit of sodium peroxide on the walls of the vessel. The reactions, $2Na + O_2 \rightarrow 2NaO$ and $Na + O_2 \rightarrow NaO + O$ do not occur to any appreciable extent. The electrical conductivity of the gas mixture does not increase as a result of the oxidation.

Bawn and Evans have studied the above reactions over a wider range of carrier-gas pressures, the experimental method being that of Hartel and Polanyi with the improvements recommended by Heller.[40] Their results are given in Table I.

TABLE I. - REACTION OF SODIUM VAPOUR WITH OXYGEN AT 260°C.

Pressure of Na at nozzle mm. × 10^3	Rate of flow of N_2 mol./sec.10^8	Rate of flow of O_2 mol./sec.10^8	Total pressure in reaction vessel mm.	Partial pressure of O_2 mm.	Diffusion coefficient of Na mol./cm.^{2}/sec.	Radius of flame cm.	Velocity constant k c.c.mol.$^{-1}$sec.$^{-1}$
1·64	3196	28·08	5·46	0·048	93·06	1·75	2·55.10^{11}
1·64	3220	5·02	10·21	0·016	49·78	1·75	4·08.10^{11}
1·64	3174	4·55	10·82	0·016	46·97	1·75	3·95.10^{11}
1·64	3227	1·38	16·20	0·007	31·37	1·75	5·90.10^{11}
1·64	3270	0·49	24·00	0·004	21·18	1·75	7·64.10^{11}

Bawn and Evans confirm that at low nitrogen pressures a termolecular reaction occurs and that the velocity constant varies linearly with the inert gas pressure. An associated complex molecule, NaO_2^*, which carries the heat of reaction as internal energy, is first formed: $Na + O_2 \rightarrow NaO_2^*$; the life-time of this complex is probably about 10^{-9} seconds and it may dissociate thus: $NaO_2^* \rightarrow Na + O_2$ or be stabilized by subsequent collision with a nitrogen molecule: $NaO_2^* + N_2 \rightarrow NaO_2 + N_2$, the nitrogen carrying away the energy of the reaction. At higher inert gas pressures the reaction changes over to a simple bimolecular reaction. In the following equations, A and B are the reactants, C is the 'third' body, nitrogen, and k_1, k_2, k_3 the individual velocity constants: $A + B \rightarrow AB^*(k_1)$; $AB^* \rightarrow A + B(k_2)$; $AB^* + C \rightarrow AB + C^*(k_3)$; $k_1(A)(B) - k_2(AB^*) - k_3(AB^*)(C) = 0$. The measured rate of reaction, $d(AB)/dt = k_3(AB^*)(C) = k_1(A)(B) - k_2(AB^*)$. When the pressure of C is high,

k_2 is small and $d(AB)/dt = k_1(A)(B)$ *i.e.* the reaction is bimolecular; and these conditions have been realized by Bawn and Evans.[41]

From a study of the vapour pressure of sodium monoxide, Brewer and Margrave have shown that the vapour consists predominantly of sodium atoms and oxygen molecules. At 1350°K. a mixture of sodium and oxygen gases at 1mm. pressure is calculated to be thermodynamically stable while a mixture at 1atm. pressure is stable above 2100°K. and should not undergo reaction.[42] Theoretical calculations of the stability of solid and gaseous alkali oxides indicate that at 1000°K. all the gaseous alkali oxides except lithium monoxide are unstable with respect to dissociation.[43]

In a limited amount of water, e.g. when small particles of sodium adhere to the sides of a beaker above the water level, a blue coloration is observed owing to the solution of the metal in water. No such colour is produced when sodium is rubbed on ice.[44] Sodium begins to react with ice at -98°C.; with water the reaction is vigorous and may be explosively so when large surfaces are involved.

The sodium-water reaction may be expressed by either or both of the following equations: $2Na + H_2O \rightarrow Na_2O + H_2 + 31{\cdot}08$ kg.-cal. per mole at 25°C.; $Na + H_2O \rightarrow NaOH + 0{\cdot}5H_2 + 33{\cdot}67$ kg.-cal. per mole at 25°C. The reaction will proceed to give sodium hydroxide and hydrogen as long as the temperature is below the melting point of sodium hydroxide, even if excess sodium is present. If, however, the temperature is raised above this value, sodium hydroxide will react with additional sodium to form sodium monoxide and hydrogen.[33]

Thermodynamic data for the reaction of steam on liquid sodium are as follows: $Na(l) + HOH(g) \rightarrow NaOH(c) + 0{\cdot}5H_2(g)$; $\Delta H^\circ_{298} = -45{\cdot}7$ kg.-cal./mole; $\Delta H^\circ_{400} = -45{\cdot}56$; $\Delta H^\circ_{500} = -44{\cdot}87$; $\Delta F^\circ_{298} = -37{\cdot}4$ kg.-cal./mole; $\Delta F^\circ_{400} = -34{\cdot}00$; $\Delta F^\circ_{500} = -28{\cdot}91$.[33]

The heat of reaction of sodium with an infinite quantity of water at 25°C. has been determined by Ketchen and Wallace as -44·35 ± 0·7 kg.-cal. per g.-atom of sodium. The heat of formation of aqueous sodium hydroxide, calculated from the above result, is −112·37 kg.-cal.[45,46] Roth and Kaule's value of -45·27 ± 0·15 kg.-cal. per g. atom of sodium at 22·4°C. and 4510 moles of water per mole of sodium hydroxide gives the heat of formation of aqueous sodium hydroxide as -113·62 ± 0·15 kg.-cal. at about 20°C.[35] The value of 44·78 ± 2·10 kg.-cal. per g. atom of sodium at 25°C. obtained by Hagen and Seiverts[47] for the reaction of sodium with an infinite quantity of water is much nearer the later figure of Ketchen and Wallace, who consider the result of Roth and Kaule too high on account of experimental error. Still more recently Messer, Ludwig and Fasolino have measured the heat of hydrolysis corrected to infinite dilution and 25°C. for the reaction: $Na(s) + H_2O(l) = NaOH(\infty) + 0{\cdot}5H_2(g)$ and found it to be: -44·23 ± 0·13 kg.-cal. per mole.[48]

For all practical purposes the reaction between sodium and water cannot be reversed; to do so would require hydrogen pressures of the order of 10^{50} atm. The estimated final isothermal and adiabatic pressures and adiabatic temperatures which would result, when 23g. of sodium is allowed to react with 2-6000g. of water at an initial temperature of 18°C. and pressure of one atm. in a rigid container, in which the hydrogen evolved must occupy the volume created by the difference between the amounts of reactants and the reaction products, are shown in Fig. 1.[33]

The reactions resulting from a leakage of water in heat transfer systems where sodium is the heat-transfer agent, have been evaluated from studies conducted at the Knolls Atomic Power Laboratory and Mine Safety Appliances Co., Callery, Pa.

The pressure, temperature and plugging effects which result from a sodium-water reaction are based on the following equations:-

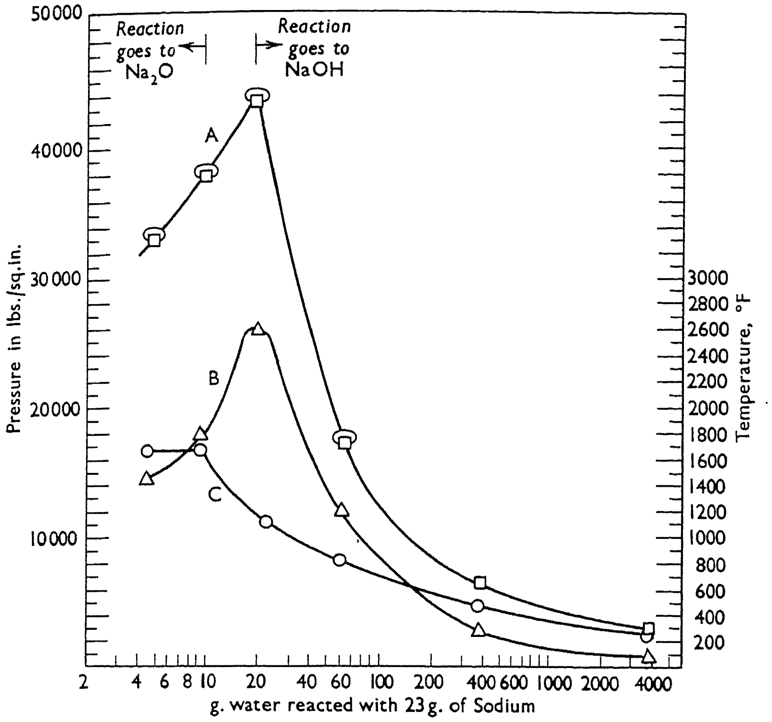

FIG. 1. ○ FINAL PRESSURE ISOTHERMAL REACTION
△ FINAL TEMPERATURE ADIABATIC REACTION
□ FINAL PRESSURE ADIABATIC REACTION
⊡ ASSUMING PERFECT GAS LAWS

(*a*) $Na(l) + H_2O(g) = NaOH(c) + 0{\cdot}5H_2(g)$ $H^\circ_{298} = -45{\cdot}7$ kg.-cal.
(*b*) $Na(l) + NaOH(c) = Na_2O + 0{\cdot}5H_2(g)$ $H^\circ_{291} = +1{\cdot}89$ kg.-cal.
(*c*) $Na(l) + 0{\cdot}5H_2(g) = NaH(c)$ $H^\circ_{298} = -13{\cdot}7$ kg.-cal.

Reaction (*a*) is extremely rapid, generally being limited only by the speed of mixing; the high sodium flow rates employed in heat-transfer systems facilitate rapid mixing and reaction. Reactions (*b*) and (*c*) are considered to be slow compared with (*a*). Should reactions (*a*) and (*b*) occur together the system pressure would be double that if reaction (*a*) occurred alone. The formation of sodium hydride would reduce the pressure build-up.

The thermal effects are largely influenced by reaction (*a*). Plugging effects arise from the fact that the solid reaction products are practically insoluble in sodium.

Three instances of leaks, which actually occurred in operating sodium-water heat exchanges, are described. In none of the leaks has there been evidence of a chemical reaction of sufficient violence to present a danger to operating personnel or adjacent equipment and in fact the sodium-water reaction of itself was not vigorous enough to indicate the leak; in each case it was detected indirectly by the plugging effects of the insoluble reaction products.

The shock effects resulting from the reaction of a water-to-sodium leak have been investigated.[33] The tests indicate that it is impossible to mix sodium and water fast enough through any conceivable leak in a heat-transfer system to obtain a reaction producing the shock waves characteristic of high explosives.

It has been shown by King[49,50] that the pressure resulting from the reaction when water is forced into sodium-potassium alloy, NaK, through a 0·25 inch pipe under a pressure differential of 200 pounds per square inch can be vented through a 1-inch relief valve set at 200 pounds per square inch. It has also been shown that the sharp pressure pulses resulting when the system is at room temperature are reduced as the temperature is increased. It is not expected that severe pressure pulses would result from leaks in heat-transfer systems operating at 600°F. or higher, since with sodium-potassium alloy initially heated to 600°F. the reaction with water proceeds to completion without pressure surges and the maximum pressure is essentially limited to the relief valve setting. Tests have also been carried out where sodium is in excess; in this case the pressure rise is reduced because of the rapid formation of sodium hydride.

It appears then that the reaction between sodium and water in practical heat-transfer systems will not generally result in mechanical damage to the system because of the absence of shock waves and the relative smoothness of the reaction at normal heat-exchanger temperatures. System plugging and subsequent problems in the removal of the reaction products may occur, however, if the leak is sufficiently large. System design recommendations to minimize the effects of leakage are given.[51] A large-scale experiment, devised to simulate the effect of a small steam leak into sodium in a sodium-superheated steam heat exchanger, gives results which show that the contents of the reaction vessel at room temperature are sodium, sodium hydroxide, sodium hydride with less than 0·1% peroxide. There is no visible corrosion of the stainless steel nozzle or equipment.[52]

Water vapour, emerging from a glass capillary tube at a pressure of 0·001-0·6mm.Hg on to a surface of sodium, does not attack the metal in the immediate proximity of the jet but at some distance away; the first signs of attack are denoted by a blue coloration and in time the reaction spreads throughout the length of the sodium plug. The above effects are much less regular when the capillary is made of metal in electrical connection with sodium.[53,54] The very slight action, *i.e.* the very small proportion of effective collisions which occur when a jet of water vapour impinges on an untarnished layer of sodium in a vacuum, is much enhanced if a high potential difference is established between the sodium and an electrode placed in the jet. The metal surface is rapidly covered with a film.[55] A revolving cylinder in an evacuated space cooled to -180°C. by liquid air and exposed on one side to a jet of sodium vapour and on the diametrically opposite side to a jet of water vapour, is coated with a thin layer of sodium which is bombarded with water vapour after half a revolution. The amount of hydrogen evolved is the same as that given with a similar jet of sulphuric acid, but with water vapour there is no luminescence. The reaction with water vapour may be trimolecular resulting in the direct formation of hydrogen molecules.[56]

The separation of hydrogen isotopes by displacement reactions of sodium with water, acids or bases has been described by several workers.[57-61] The metal is dissolved in the reagent of known deuterium content and the liberated hydrogen burned in a flame with a slight excess of oxygen. The proportion of the hydrogen isotopes in the water so formed is determined by density measurements. According to Johnston and Davis[61] the data are reproducible and confirm the applicability of the relationship, $d\ \ln(H) = \alpha d\ \ln(D)$, where (H) and (D) are instantaneous values of the amounts of protium and deuterium in the liquid phase, and α is the 'isotopic separation factor'. When the initial water contains 0·5% deuterium, the value of α at or near room temperature is 2·55–2·66. Hughes, Ingold and Wilson[59] give values of 2·8, 2·8, 3·0 and 2·9 for media ranging from strongly alkaline to strongly acidic. Horiuti and Szabo[58] obtain nearly the same value as Johnston and Davis[61] by using water vapour instead of liquid water. This implies that the reaction of sodium with liquid water occurs by a molecular and not an ionic mechanism.[61]

No reaction occurs, nor is any luminescence observed, when a freshly cut surface of sodium is exposed to the action of dry hydrogen at room temperature.[2] Pure sodium begins to absorb hydrogen appreciably at 100–110°C. and more rapidly as the temperature is raised. A mixture of sodium hydride and sodium is obtained.[62] Pure sodium hydride is obtained by leading a rapid stream of hydrogen directly on to the surface of sodium at a temperature above 350°; the sodium hydride is carried away as a white smoke which is precipitated electrically and filtered through glass wool.[63] The hydride is also prepared for use *in situ* by the action of hydrogen on high surface sodium dispersed on an inert solid, such as sodium chloride.[64] Sodium hydride may also be prepared for use *in situ*, as in the preparation of sodium borohydride (see page 498), by heating a mixture of molten sodium and a refined high boiling mineral oil agitated with a high shear in an atmosphere of hydrogen. The sodium dispersion technique increases the rate of formation of sodium hydride and the oily coating makes the sodium hydride easier to handle.[65]

Sodium has been used as a hydrogenation catalyst; it is unaffected by the usual catalyst poisons and is liquid at the temperature of the reaction. Vigorous agitation or admixture with an inert material is necessary to increase the surface of contact.[66]

From experimental values obtained over the temperature range of 289°C. to 415·5°C. the following equation has been derived for the dissociation pressure of sodium hydride: $\log p_{\text{mm.}} = -6100/T + 11{\cdot}66$.[67] Dissociation pressures have also been measured at 240–280°C.[68] and 310–380°C.[69]

Sodium hydride is quite stable when dissolved in sodium, as may be seen from Fig. 2, where a resulting stabilizing effect is observed on the normal dissociation pressure curve when, by the dissociation of sodium hydride in a mixture of metal and hydride heated in a closed system, sufficient sodium has been produced to dissolve all the remaining sodium hydride. The dissociation of sodium hydride is also depressed by the presence of an inert gas at pressures as low as 190mm.[70]

The dissociation pressure of the sodium/sodium hydride/hydrogen system has been measured at temperatures ranging from 500° to 600°C. and pressures as high as 4600 cm. and the results plotted as pressure versus composition and log p versus $1/T$. The first plot shows the isotherms as nearly horizontal lines which break away sharply at both ends of the composition axis (abscissae). The non-horizontal portions of the isotherms indicate the region of limited solubility of sodium and sodium hydride in the temperature range studied. The dissociation pressure of sodium hydride is essentially independent of the composition over the range 25 to 90% sodium hydride; the equilibrium pressures of both richer and poorer sodium-hydrogen composition phases however, are dependent on the composition, as may be seen from Table II.

The differential heats of dissociation have been calculated from the slopes of the log p versus $1/T$ plot and the following values estimated for the thermodynamic properties of sodium hydride:

$$\Delta H^{\circ}_{550} = 11{,}610 \text{ g.-cal./mole for 100\%NaH;} \quad \Delta F^{\circ}_{T} = 11{,}610 - 17{\cdot}41T;$$
$$\Delta F^{\circ}_{25} = +6{,}410 \text{ g.-cal./mole for 100\%NaH;} \quad \Delta S^{\circ}_{25} = 15{\cdot}5 \text{e.u.;}$$
$$\Delta H^{\circ}_{550} = 13{,}590 \text{ g.-cal./mole for 30–80\%NaH;}$$
$$\Delta F^{\circ}_{25} = 7{,}730 \text{ g.-cal./mole for 30–80\%NaH;} \quad \Delta S^{\circ}_{25} = 17{\cdot}7 \text{e.u. for 30–80\%NaH.}$$

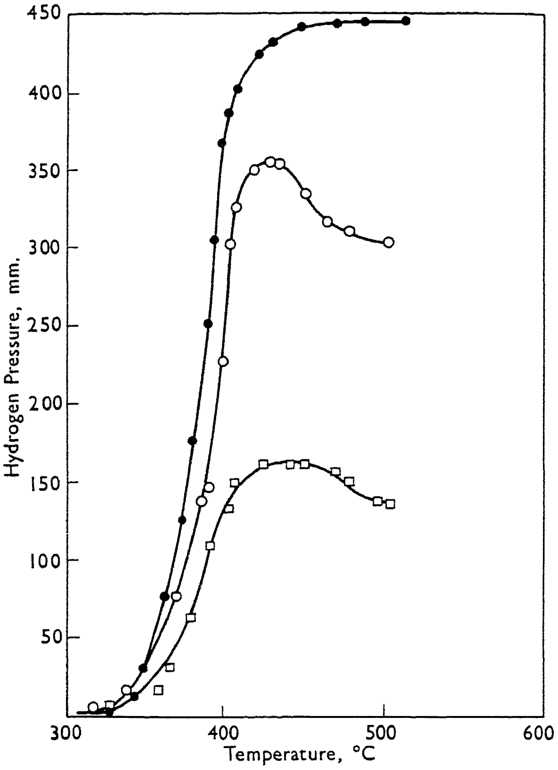

FIG. 2. THE SODIUM-SODIUM OXIDE-SODIUM HYDRIDE SYSTEM
● Na 10g. NaH 1·6g. Na_2O nil;
⊙ Na 11·5g. NaH 2·06g. Na_2O 2·33g.;
⊡ Na 11·0g. NaH 0·76g. Na_2O 2·3g.

TABLE II. - EMPIRICAL CONSTANTS FOR THE INTEGRATED CLAUSIUS-CLAPEYRON EQUATION: $\log P_{cm.} = -a/T + b$ FOR SODIUM HYDRIDE

%NaH	a	b
100	5070	9·49
90	5806	10·32
80–30	5958	10·47
20	6058	10·55
10	6222	10·70

It should be pointed out that unit activities of sodium and sodium hydride have been assumed in arriving at these data.[71] Herold gives −13·94 kg.-cal./mole for the heat of formation of sodium hydride calculated from dissociation pressure data.[67]

Other thermodynamic data given for sodium hydride are: $Na(c) + 0{\cdot}5H_2(g) \rightarrow NaH(c)$, $\Delta H(25°C.) = -13{\cdot}7$ kg.-cal./mole; for NaH(g), $\Delta H(25°C.) = -29{\cdot}88$ and $\Delta F(25°C.) = -24{\cdot}78$ kg.-cal./mole.[34] The heat of formation of sodium hydride calculated from the heat of hydrolysis of sodium and water corrected to infinite dilution and 25°C.: $Na(c) + H_2O(l) = NaOH(\infty) + 0{\cdot}5H_2(g) + 44{\cdot}23 \pm 0{\cdot}13$ kg.-cal./mole and from the heat of hydrolysis of sodium hydride and water corrected to infinite dilution and 25°C.: $NaH(c) + H_2O(l) = NaOH(\infty) + H_2(g) + 30{\cdot}63 \pm 0{\cdot}23$; has been found to be −13·60 ± 0·27 kg.-cal./mole.[48] The heat of formation of sodium hydride at constant pressure at 25°C. is given as −15·69 ± 0·12 kg.-cal./mole.[72]

Yasumori and Sato[73] have criticized Golden's reaction-rate theory when applied to the reaction $NaH + H \rightarrow Na + H_2$.

'Active' hydrogen reacts with sodium at −40°C., the 'active' hydrogen being produced by passing an electric discharge through hydrogen at a low pressure in the presence of sodium. With an initial hydrogen pressure of 743×10^{-3}mm.Hg, an accelerating potential of 94V. and a steady current of 546 microamp., the amount of hydrogen absorbed by sodium when the discharge is passed for ten minutes is such that the pressure is reduced to 336×10^{-3}mm. On heating the tube to 300°C. a volume of gas is liberated which is always less than the original volume absorbed and the absorption and evolution of hydrogen may be continued until finally a stage is reached when no further absorption occurs. The gas pressure is then 96×10^{-3}mm.Hg. When a lower accelerating potential is used, 54V., the final pressure is 202×10^{-3}mm.Hg. A modified apparatus which permits the absorption of larger amounts of hydrogen has been used to obtain sufficient reaction product for identification and it has been shown that with sodium–potassium alloy at −40°C. and an accelerating potential of 600V. the white crystalline material produced on the surface of the alloy is a mixture of sodium and potassium hydrides. A similar absorption of hydrogen by sodium occurs when the gas is ionized by α-rays from polonium.[74]

'Active' hydrogen is produced when (*a*) sodium is saturated with hydrogen at 200°C. and the temperature then raised until gas is liberated; (*b*) sodium is treated with hydrogen at 670°C.; (*c*) sodium is treated with hydrogen at 380°C. and the sodium hydride condensed and decomposed by water saturated with hydrogen.[75] Sodium vapour is excited to luminescence when exposed to Wood's 'active' hydrogen, *i.e.* atomic hydrogen produced by maintaining a powerful electric discharge through a long tube through which moist hydrogen is streamed at low pressures.[76] When an electric discharge excited by 5000V. is passed through a tube in which hydrogen at 0·05 to 0·1mm.Hg is streaming at a flow rate of about 1 litre/sec. and the gas then passed via a nozzle of 1 mm. diameter into a mixing chamber containing sodium vapour at about 0·1mm. pressure, a diffuse yellow glow becomes conspicuous at about 200°C. At higher temperatures the intensity of the light increases and is concentrated near the nozzle. Only the *D* line of sodium is present. It is considered that a three-body collision of two hydrogen atoms and a sodium atom takes place and part of the energy of recombination is expended in producing excitation of the metal atom.[77] Some chemiluminescence and quenching reactions of sodium in atomic hydrogen are described by Magee and Taikei.[78]

The linkage of atoms in a number of hydrides, including lithium and sodium hydrides, has been investigated by Tomiska, who has determined or computed the bonding forces, the distance separating the atoms and the character of the bonds. The force binding the atoms is a linear function of the number of external electrons in the molecule.[79]

References occur in the literature to the following compounds of sodium and mercury: Na_5Hg,[80] Na_3Hg,[80-85] Na_5Hg_2,[83-85] Na_3Hg_2,[81,83,84] $NaHg$,[81-84] Na_7Hg_8,[81,83,84] $NaHg_2$,[81-84,86] $NaHg_4$,[81-84,86] $NaHg_5$,[87] $NaHg_6$,[86,88] $NaHg_{16}$.[86]

The melting points of the amalgams, compiled by Biltz, Weibke and Eggers[84] are: Na_3Hg 35°C.; Na_5Hg_2 66°C.; Na_3Hg_2 119°C.; $NaHg$ 212°C.; Na_7Hg_8 222°C.; $NaHg_2$ 354°C.; $NaHg_4$ 156°C.

The heats of formation in g.-cal. per g.-atom of mercury of the following amalgams have been measured by means of a Bunsen ice calorimeter and are given in brackets: Na_3Hg(9·3); Na_3Hg_2(10·4); NaHg(11·3); Na_7Hg_8(10·6); $NaHg_2$(9·4); $NaHg_4$(5·6). The heat required to split off one g.-atom of liquid mercury from a mercury-rich compound to give the next lower one is: $NaHg_4$ −1·9; $NaHg_2$ −7·8; Na_7Hg_8 −5·3; NaHg −13·2; Na_3Hg_2 −11·4; Na_3Hg −9·3. These amalgams are definite chemical compounds immiscible or only slightly miscible with an excess of their components.[81]

The appearance of the following sodium-mercury compounds has been described: Na_3Hg, lustrous silvery flakes; NaHg, sparkling metallic needles with a pronounced reddish tinge; $NaHg_2$, silvery white crystals; $NaHg_4$, small lustrous silvery crystals.[82]

Liquid ammonia solutions of sodium react with mercuric iodide and cyanide and with mercurous iodide to form the compound NaHg which decomposes to sodium and the compound $NaHg_2$ (see page 515).

Sodium ignites in fluorine,[33] but when the gas is liquefied there is no reaction.[89] The metal may be distilled in dry chlorine without reaction.[90]

The following thermodynamic data are given for the reaction of sodium with the halogens: Na(c) + 0·5F_2(g) → NaF(c), ΔH°_{298} = −136·0; ΔF°_{298} = −129·3; Na(c) + 0·5Cl_2(g) → NaCl(c), ΔH°_{298} = −98·23, ΔH°_{500} = −98·75, ΔF°_{298} = −91·79, ΔF°_{400} = −90·23, ΔF°_{500} = 87·97; Na(c) + 0·5Br_2(l) → NaBr(c), ΔH°_{298} = −86·03; Na(c) + 0·5I_2(c) → NaI(c), ΔH°_{298} = −68·84, ΔH and ΔF being expressed as kg.-cal./mole.[33,91]

Chlorine prepared by the action of sulphuric acid on a mixture of sodium chloride and manganese dioxide is found, after passage over potassium permanganate and a drying agent, to react with solid sodium almost as rapidly as moist air. A white reaction product is formed but no luminescence occurs. The reaction with bromine vapour is similar, whereas no reaction occurs with iodine, probably because its vapour pressure is too low at 20°C.[2]

Haber and Zisch have observed that when sodium vapour is allowed to react with chlorine diluted with nitrogen at atmospheric pressure so that the temperature is kept below that at which black-body radiation occurs, a reaction luminosity becomes faintly visible at 340°C. and the *D*-lines of sodium are easily seen at 473°C.[37]

The rate of reaction of sodium atoms with the halogens has been measured by the 'highly dilute flame' method, so called because the reaction is chemiluminescent. The method is particularly suitable for those reactions which occur at almost every collision. The reacting vapours are introduced at opposite ends of an evacuated tube at a pressure of about 10^{-3}mm.Hg and a temperature at which sodium vapour is largely dissociated into atoms. The reaction zone is several centimetres in length and the extent of the reaction is greater at the centre where most penetration occurs. The density of the distribution of the solid product deposited on the walls of the tube, and of the chemiluminescence produced, can be measured with accuracy and the velocity of the reaction estimated by analysis of the distribution of the reaction products. This method has been used to investigate the reaction of sodium vapour with chlorine, bromine and iodine.[92-97]

The luminescence produced in the sodium-halogen reaction has been examined in greater detail by introducing the halogen from a nozzle or jet into an excess of sodium vapour. The light distribution curve does not coincide with the precipitate-distribution curve and it is inferred that the reaction takes place in two stages: (*a*) Na + Cl_2 → NaCl + Cl + 40·7 kg.-cal., (*b*) Cl + Na_2 → NaCl + Na + 80 kg.-cal., (*c*) Na + Cl → NaCl + 97·5 kg.-cal.; reaction (*c*) occurring on the walls of the reaction vessel. In the absence of a 'third' body, the reaction between sodium and chlorine atoms takes place only once in 10,000 collisions. The heats of reaction given in (*a*), (*b*) and (*c*) are not those given by the original workers, Bogdandy and Polanyi[96] but are recalculated from more recent data.[97] The luminescence accompanying the reaction is considered to result from the secondary reaction (*b*) because the intensity of the luminescence is diminished and almost completely extinguished by raising the temperature of the reaction zone, thus decreasing the number of sodium molecules present and increasing the number of sodium molecules dissociated into atoms. The chances for reaction (*b*) to proceed are therefore minimized by raising the temperature and it would appear that the luminescence is produced by the sodium chloride molecules formed in (*b*) carrying most of the energy of the reaction, colliding with other sodium atoms and exciting them to emission of the *D*-line; (*b*) $Cl + Na_2 \rightarrow NaCl^* + Na$; $NaCl^* + Na \rightarrow NaCl + Na^*$; $Na^* \rightarrow Na + h\nu$. This view has been confirmed, by quenching experiments with nitrogen.[92] All the gas reactions occur without activation energy.[96,97]

The reactions with bromine are: (*a*) $Na + Br_2 \rightarrow NaBr + Br + 40$ kg.-cal., (*b*) $Na_2 + Br \rightarrow NaBr + Na + 68$ kg.-cal., (*c*) $Na + Br \rightarrow NaBr + 86$ kg.-cal. As in the chlorine reaction the light yield is diminished by increasing the temperature of the reaction zone.[94]

Sodium vapour and iodine behave similarly: (*a*) $Na + I_2 \rightarrow NaI + I$; (*b*) $Na_2 + I \rightarrow NaI + Na + 54$ kg.-cal.; (*c*) $Na + I \rightarrow NaI + 68{\cdot}7$ kg.-cal. Again the light intensity is diminished by raising the temperature of the reaction zone.[93]

Sodium atoms react more readily with chlorine than with iodine atoms and this is in agreement with the thermodynamic values for the heats of dissociation of the sodium halides, calculated at absolute zero: NaCl 93·4 kg.-cal., NaBr 85·8 kg.-cal., NaI 68·7 kg.-cal.[93]

According to Nishibori the iodine molecule and sodium atom do not combine unless they approach in the region of dynamic collision in the sense of the dynamic theory of gases.[98]

The chlorine atoms, formed in the primary reaction when sodium atoms are present in a mixture of chlorine and hydrogen, induce a chain reaction by means of which several thousand molecules of hydrogen chloride are formed for each sodium atom reacting: $Na + Cl_2 \rightarrow NaCl + Cl$; $Cl + H_2 \rightarrow HCl + H$; $H + Cl_2 \rightarrow HCl + Cl$ and so on.[99,100]

In a similar manner the inducing effect of sodium atoms in a mixture of chlorine and methane is demonstrated: $Na + Cl_2 \rightarrow NaCl + Cl$; $Cl + CH_4 \rightarrow CH_3 + HCl$; $CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$ and so on.[97]

The reactions of atomic sodium with halogens, halogen acids and alkyl halides are discussed from a kinetic point of view by Polanyi[101] and the mechanism of the reaction between sodium vapour and chlorine gas studied by means of molecular beams.[102]

A spectroscopic investigation of chemiluminescence observed when iodine is allowed to react in the vapour phase with sodium has been carried out by Lyalikov and Terenin[103] and the excitation of spectral lines by the action of sodium vapour with the halogens has been described.[103-106] Franck and Gibson[107] have studied the extinction of the *D*-lines in sodium flames by the addition of chlorine. The theory of the diffusion flame method for fast reactions with sodium atoms has recently been discussed by Reed and Rabinovitch.[108]

An energy diagram of sodium chloride has been constructed from curves representing the interaction energy of sodium and chlorine ions and atoms in the gaseous state and in solution.[109]

Molten iodine monochloride added dropwise to sodium wire reacts vigorously at first with the formation of sodium chloride; with small sticks of sodium there is a slight evolution of heat. The reaction is incomplete.[110] A slight heat of reaction is observed when molten iodine monobromide is added dropwise on to sodium in sticks; there is about 1% conversion to sodium bromide. Iodine monobromide is more reactive than iodine but less so than iodine monochloride.[111] A mixture of sodium and iodine monobromide explodes when subjected to shock by striking with a hammer.[112]

Hydrogen chloride prepared by dehydrating concentrated hydrochloric acid with sulphuric acid reacts very vigorously with sodium wire, converting it to sodium chloride; no luminescence accompanies the reaction.[2] An electron diffraction study of the white coating formed on the surface of sodium by the action of hydrogen chloride shows the presence of crystalline sodium chloride.[113]

Thermodynamic data for the reactions of sodium with the hydrogen halides are given below:-[33]

$$\begin{gathered} \mathrm{Na(c)} + \mathrm{HF(g)} \rightarrow \mathrm{NaF(c)} + 0{\cdot}5\mathrm{H_2(g)},\ \Delta H^\circ_{298} = -71{\cdot}8, \\ \Delta F^\circ_{298} = -64{\cdot}6;\ \ \mathrm{Na(c)} + \mathrm{HCl(g)} \rightarrow \mathrm{NaCl(c)} + 0{\cdot}5\mathrm{H_2(g)}, \\ \Delta H^\circ_{298} = -76{\cdot}169,\ \Delta F^\circ_{298} = -69{\cdot}016; \\ \mathrm{Na(c)} + \mathrm{HBr(g)} \rightarrow \mathrm{NaBr(c)} + 0{\cdot}5\mathrm{H_2(g)},\ \Delta H^\circ_{298} = -81{\cdot}370; \\ \mathrm{Na(c)} + \mathrm{HF(g)} \rightarrow \mathrm{NaF(c)} + 0{\cdot}5\mathrm{H_2(g)},\ \Delta H^\circ_{298} = -75{\cdot}04. \end{gathered}$$

In the above reactions, ΔH and ΔF are expressed as kg.-cal./mole.

Atomic reactions of sodium with hydrogen chloride carried out by the highly dilute flame method (described on page 450) are accompanied by chemiluminescence: $\mathrm{Na} + \mathrm{HCl} \rightarrow \mathrm{NaCl} + \mathrm{H} - 5$ kg.-cal. The reaction velocities increase from hydrogen chloride to hydrogen iodide.[114] The above reactions require no activation energy.[115]

The rates of reaction of sodium atoms with hydrogen chloride and deuterium chloride have been measured by the diffusion flame method.[38,97] This method is particularly applicable to reactions which do not occur at almost every collision. Surface reactions are minimized by introducing the reactants in an inert gas so that the rate of diffusion is such that the sodium vapour leaving a nozzle is used up before it reaches the walls of the vessel. The distance to which the sodium penetrates is determined by a sodium resonance lamp. For the reaction: $\mathrm{Na} + \mathrm{HCl} \rightarrow \mathrm{NaCl} + \mathrm{H}$, the rate is 0·412c.c. per mole per sec. and for $\mathrm{Na} + \mathrm{DCl} \rightarrow \mathrm{NaCl} + \mathrm{D}$, it is 0·344c.c. per mole per sec. The activation energies calculated from the rates are 6·1 and 6·4 kg.-cal. respectively *i.e.* they differ by about 300 g.-cal. which is approximately equal to the difference between the zero-point energies in the initial and critical transition states of hydrogen chloride and deuterium chloride.[116]

Chlorine peroxide in aqueous solution is reduced by sodium amalgam to sodium chlorite: $\mathrm{Na} + \mathrm{ClO_2} \rightarrow \mathrm{NaClO_2}$. The technical and economic aspects of the process, first patented by Finnois[117] have been reviewed by Nicolai.[30] The reactions which can take place are (*a*) $\mathrm{ClO_2} + e \rightarrow \mathrm{ClO_2^-}$; (*b*) $\mathrm{Na(Hg)} \rightarrow \mathrm{Na^+} + \mathrm{Hg} + e$; (*c*) $\mathrm{ClO_2^-} + 2\mathrm{H_2O} + 4e \rightarrow \mathrm{Cl^-} + 4\mathrm{OH^-}$; (*d*) $2\mathrm{Hg} \rightarrow \mathrm{Hg_2^{++}} + 2e$; (*e*) $2\mathrm{H^+} + 2e \rightarrow \mathrm{H_2}$; (*f*) $2\mathrm{ClO_2} + 2\mathrm{OH^-} \rightarrow \mathrm{ClO_2^-} + \mathrm{ClO_3^-} + \mathrm{H_2O}$; (*g*) $8\mathrm{H^+} + 8\mathrm{ClO_2^-} \rightarrow 6\mathrm{ClO_2^-} + \mathrm{Cl_2} + 4\mathrm{H_2O}$. Optimum experimental conditions which favour reactions (*a*) and (*b*) and minimize reactions (*c*)–(*g*) result in a yield of more than 95% of a 20% sodium chlorite solution.

Sodium is attacked by the fumes of nitric acid at 15°C. and sodium nitrate is formed.[118] The action of nitric acid vapour has also been examined by mixing the acid with twice its volume of sulphuric acid and heating the mixture on a hot plate; previously dried air is passed over the surface of the acid into an observation chamber containing sodium at ordinary temperature. A slight glow is observed when the acid is heated at 40°C. and the light intensity increases as the temperature is raised to 85°C. The reaction is somewhat greater than with moist air.[2]

A very faint glow is observed when sodium is acted upon by previously dried air which has been passed over the surface of glacial acetic acid at

105°C. and through a calcium chloride tube into an observation chamber containing sodium wire.[2]

The heats evolved when solid sodium is acted upon by acetic and sulphuric acids are 53·7 and 68·5 kg.-cal./mole respectively, the values referring to the formation of the compounds in the liquid state.[119]

The reaction of sodium atoms with sulphuric acid vapour has been studied by allowing a jet of sodium vapour to impinge on one side of a cylindrical revolving drum in an evacuated enclosure and a jet of sulphuric acid vapour on the diametrically opposite side, the cylinder being cooled by liquid air to -180°C. Only the uppermost layer of sodium reacts with the acid forming a monomolecular protective layer of sodium hydrogen sulphate. The liberated hydrogen is evolved as atomic hydrogen, the reaction being accompanied by luminescence.[56]

Thomas and Rule[120] give the following solidification temperatures for the compounds and eutectic mixtures found in the sodium–sulphur system; Na_2S, >800°C.; Na_2S_2, 445·0°C.; Na_2S_2-Na_2S_3, eutectic, 206·0°C.; Na_2S_3, 223·5°C.; Na_2S_3-Na_2S_4, eutectic, 222·6°C.; Na_2S_4, 275·0°C.; Na_2S_4-Na_2S_5, eutectic, 247·6°C.; Na_2S_5, 251·8°C.; a saturated solution of sulphur in sodium pentasulphide solidifies at 249·6°C.

Pearson and Robinson[121] have confirmed the presence of the di-, tetra- and penta-sulphides in the sodium–sulphur system and give the following solidification temperatures: Na_2S, 978°C., stable at its melting point; Na_2S_2, 473·9°C., decomposes slightly at its melting point; Na_2S_4, 284·8°C., remarkably stable at its melting point. The upper arrest point for the pentasulphide is 254°C. The solid which separates out in the trisulphide area has a pearlite structure typical of a eutectic mixture; it is considered that sodium trisulphide decomposes at its melting point to give a mixture of di- and tetrasulphide. A phase diagram for the system[121a,b] is shown in Fig. 3.

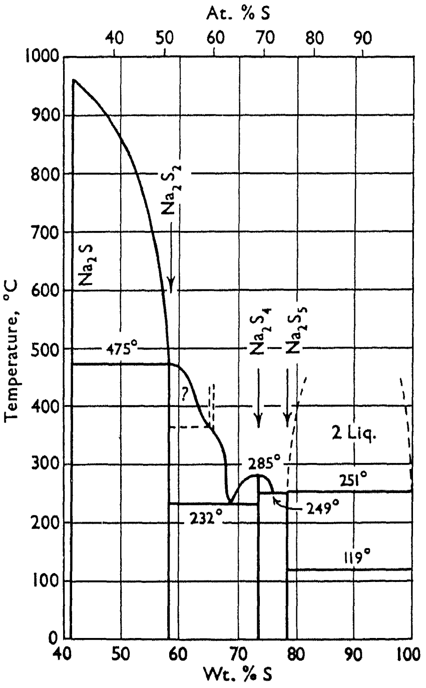

FIG. 3. EQUILIBRIUM DIAGRAM FOR Na-S SYSTEM

Neither Thomas and Rule nor Pearson and Robinson have found any indication of the tetrasodium compounds, Na_4S_3, Na_4S_5, Na_4S_7, Na_4S_9, described by Friederich and Mousset.[122] The compounds, Na_2S_3, Na_2S_6, and Na_2S_7, which cannot be obtained in the solid state from molten mixtures, have been shown to exist in liquid ammonia solution[123] (see also page 510).

Fehér and Berthold,[124] by modifying the procedure described in [121,125], have prepared sodium tetrasulphide by heating a solution of sodium in ethanol, saturated with hydrogen sulphide, with sulphur, and removing the alcohol under reduced pressure.

Anhydrous sodium disulphide is formed when an alcoholic solution of sodium tetrasulphide, (prepared from 4·95g. of sodium in 150ml. of alcohol and 10·35g. of sulphur) is reduced with small pieces of sodium, total weight 9·5g.[124]

The preparation of polysulphides by the action of sodium on molten sulphur is unsatisfactory because the reaction is so violent. Locke and Austell[126] found that the reaction could be modified by allowing the elements to react under boiling toluene but that under these conditions only the trisulphide with some tetrasulphide could be obtained. Draves and Tartar[127] treated excess sulphur in boiling toluene with sodium, using an atmosphere of hydrogen to exclude air and moisture, and found that in the product, which had been dried overnight at 20mm. pressure in an atmosphere of hydrogen, the atomic ratio of sulphur to sodium was 2·989:2, 3·007:2, 3·091:2 and 3·172:2 in four tests. Pearson and Robinson[121] have observed that when clean sodium is melted in dried toluene, heated under reflux, and sulphur added in 0·5g. portions, the sodium is immediately coated with a yellow coherent film, and when 1·5 atomic proportions of sulphur have been added the film bursts and the escaping sodium reacts vigorously with the dissolved sulphur. It is necessary to cool the flask with water; otherwise a small amount of carbon is produced. After boiling for a further 20 minutes to complete the reaction, the product is quickly filtered, washed with cold toluene and dried at 100°C. for 2 hours under a good vacuum. It would appear that the first product formed in the above reaction is a polysulphide, because even when only a trace of sulphur is used there is no indication of a white film, which would be present if sodium monosulphide were formed; instead, the metal surface is partially coated with distinctly yellow patches. However much sulphur is used, no compound other than the trisulphide is formed.

More recently Fehér and Berthold[124] have repeated the above work and shown that when the amount of sulphur used is that required for the formation of the trisulphide, the product contains a small amount of free sodium, *i.e.* a polysulphide higher than the trisulphide is formed. When the requisite amount of sulphur for the pentasulphide is used, the product has the composition of $Na_2S_{3\cdot5}$ or $Na_2S_{3\cdot3}$.

The hydrates, $Na_2S_2,6H_2O$, $Na_2S_3,8H_2O$, $Na_2S_4,8H_2O$, $Na_2S_4,9H_2O$, Na_2S_4,-$11H_2O$ and $Na_2S_5,6H_2O$ have been prepared by Pearson and Robinson[121] by converting sodium to sodium monosulphide in aqueous alcoholic solution, treating the solution with the theoretical amount of sulphur and cooling in freezing mixtures.

Sodium sulphide is produced by dissolving sulphur in an aqueous solution of sodium sulphide, *i.e.* in some of the product, and reducing the polysulphide with sodium amalgam to sulphide. The economic aspect of this process is discussed by Nicolai.[30]

A method of investigating chemical reactions in the solid phase is described by Semenov and Shalnikov,[128] the reactants being sodium and sulphur. The two substances are evaporated simultaneously on to a surface cooled with liquid air and enclosed in a high vacuum so that an extremely intimate mixture is formed. When the evaporated layer becomes so thick that its surface is above a certain critical temperature, a very rapid reaction occurs in an elliptical zone having its centre approximately at the point of thickest deposit, and proceeds inwards towards the surface cooled with liquid air spreading sideways from the thickest point, the heat of reaction warming the interior to the critical temperature.

A low pressure reaction between sodium atoms and sulphur occurs at and above 300°C. and is accompanied by chemiluminescence, the *D*-lines of sodium being displayed with a continuous background.[129]

Sodium dispersions are used to remove sulphur compounds, including thiophen, from petroleum.[130]

The solubility of selenium in sodium is given by the expression, $w = -8{\cdot}4 + 0{\cdot}0858t$ where w = wt.-% and t = °C.[33]

Sodium reacts with selenium in liquid ammonia to form the compounds: Na_2Se, Na_2Se_2, Na_2Se_3, Na_2Se_4, Na_2Se_5 and Na_2Se_6,[123] (see also page 511).

The phase diagram prepared by thermal analyses by Mathewson in 1907 does not include the compound Na_2Se_5.[131]

Chemiluminescence is observed in the low pressure reaction between sodium atoms and selenium at and above 300°C.[129]

Sodium reacts slowly in the cold with selenium monochloride forming sodium chloride and selenium; the reaction soon stops, however, owing to the presence of insoluble sodium chloride. On heating, the reaction proceeds vigorously with the evolution of light and heat.[132]

Potentiometric titrations of tellurium with a liquid ammonia solution of sodium give points of inflexion at compositions corresponding to: Na_2Te, Na_2Te_2, Na_2Te_3, Na_2Te_4.[123] For details of reactions in liquid ammonia, see also page 511.

Kraus and Glass[133] have measured the electrical resistance of liquid mixtures of sodium telluride, Na_2Te, and tellurium at concentrations up to 54at.-% of sodium and temperatures up to 500°C. It is inferred that sodium and tellurium form a compound Na_2Te_6 which has a congruent melting point at 436°C. A phase diagram for the system[121a,b] is shown in Fig. 4.

Sodium and tellurium are completely miscible in the liquid phase, and in addition to the normal telluride, Na_2Te, two other compounds, Na_2Te_2 and Na_2Te_6, are formed as well as two eutectics, Na_2Te–Na_2Te_6 and Na_2Te_6–Te. The transition point for Na_2Te_2 and Na_2Te lies at 355°C.[134]

The solubility of tellurium in sodium up to 700°C. is given by the equation: $w = -8{\cdot}1 + 0{\cdot}083t$ where w = wt.-% and t = °C.[33]

Kraus and Ridderhof[135] give the heats of formation of the compounds, Na_2Te and NaTe, as 28·1 and 25·4 kg.-cal./g.-atom respectively from measurements made of the heats of reaction and heats of solution in liquid ammonia at −34°C.

Although a vigorous reaction occurs when liquid tellurium is poured over solid sodium, Kubaschewski[136] has been able to measure the heat evolved by carrying out the reaction in an atmosphere of argon: the results given in Table III enable the heats of formation of the compounds Na_2Te, NaTe and

TABLE III. - HEATS OF FORMATION: SODIUM-TELLURIUM SYSTEM

Atom % Te	Heat of formation, kg.-cal./g.-atom
87·0	3·7
79·2	6·4
67·0	8·3
65·3	8·8
46·6	15·9
44·1	18·0

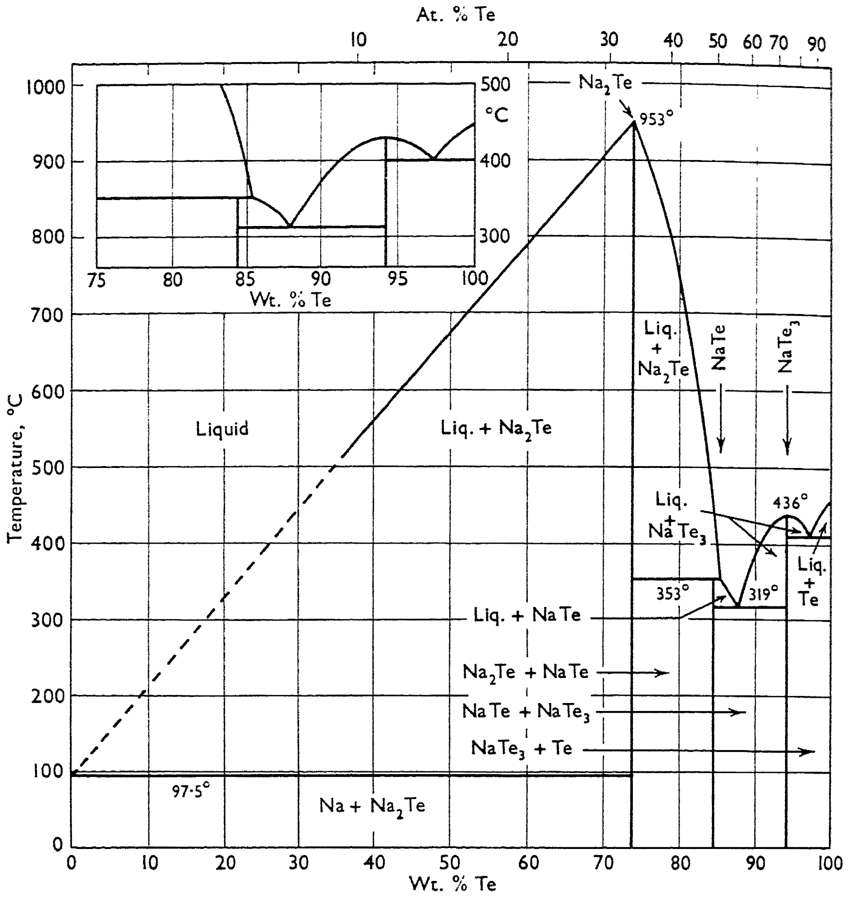

FIG. 4. EQUILIBRIUM DIAGRAM FOR Na-Te SYSTEM

$NaTe_3$ to be calculated as: 20 ± 2; 15 ± 1·5 and 7·5 ± 0·8 kg.-cal./g.-atom, respectively.

A very faint characteristic greenish-blue light is emitted when dry hydrogen sulphide is passed over sodium wire. With moist hydrogen sulphide a very rapid reaction occurs, sufficient heat being produced to melt the sodium.[2]

For the reaction: $2Na(c) + H_2S(g) \rightarrow Na_2S(c) + H_2(g)$, $\Delta H^\circ_{298} = -84{\cdot}385$ kg.-cal./mole.[33]

The rate of reaction of sodium atoms with hydrogen sulphide has been studied by the diffusion flame method as already described for oxygen (see page 442) with the results given in Table IV.

The mechanism of the reaction is given by the following equations: (*a*) $Na + H_2S \rightarrow NaH_2S^*$; (*b*) $NaH_2S^* \rightarrow Na + H_2S$; $NaH_2S^* + N_2 \rightarrow NaH_2S + N_2^*$. At low inert gas pressures, the rate of the reaction is determined by a three-body collision, the nitrogen carrying away the energy of the reaction. At high nitrogen pressures reaction (*b*) does not occur to any appreciable extent and the reaction becomes bimolecular.[41]

Sodium reacts quite readily with dry ammonia at room temperature to form sodamide and hydrogen; the reaction is not accompanied by luminescence.[2] At 300°C., molten sodium reacts rapidly, and the reaction may be utilized to

TABLE IV. - REACTION OF SODIUM VAPOUR WITH HYDROGEN SULPHIDE AT 238°C.

Reaction partner	Pressure of Na at nozzle mouth mm. × 10^3	Rate of flow of N_2 mol./sec. 10^8	Rate of flow of H_2S mol./sec. 10^8	Total pressure in reaction vessel mm.
H_2S	3·873	8,932	454	11·31
	4·227	10,560	867	14·45
	4·613	9,999	1·543	12·77

Partial pressure of H_2S mm.	Diffusion coefficient of Na in N_2 mol./cm.$^{-2}$/sec.	Radius of flame cm.	Velocity constant c.c.mol.$^{-1}$sec.$^{-1}$
0·548	42·20	1·33	3·45 × 10^{10}
1·095	33·02	0·94	3·91 × 10^{10}
1·705	37·38	1·00	2·45 × 10^{10}

clean up equipment containing sodium residues. The amide decomposes at higher temperatures to give sodium, sodium hydride, nitrogen and hydrogen.[33]

Sodium vapour has a negative catalytic effect on the decomposition of ammonia in a glow discharge.[137]

Sodium dissolves in liquid ammonia to give intense blue solutions and in the absence of catalysts and at ordinary temperatures a slow reaction occurs resulting in the formation of sodamide and hydrogen. The heavier the alkali metal the more readily it reacts with liquid ammonia; under comparable conditions the times of reaction are: lithium and sodium several days, potassium 60 minutes, rubidium 30 minutes, caesium 15 minutes.[138]

Liquid ammonia solutions of sodium exposed to short ultra-violet light (2144–2550 A.) give off hydrogen and the sodium is converted into sodamide. The intense blue colour of liquid ammonia solutions of sodium fades rapidly on exposure to the intense radiation from a quartz-mercury lamp, and a pale yellow solution of the amide is produced. Illumination for a few minutes with the full radiation from a cadmium spark results in the development of considerable gas pressure.[139]

Burgess and Kahler have studied the catalytic effect of silver, zinc, nickel, thallium, iron and platinum on the reaction between sodium and liquid ammonia at its boiling point, and found that platinized platinum, nickel, rusted iron and ferrous oxide are the most efficient catalysts. As adsorbed air films reduce the effectiveness of the catalyst, the apparatus should be evacuated before introducing ammonia. Increase of rate of stirring increases the rate of reaction but no further effect is observed at a rate above 250 r.p.m. The accumulation of sodamide in solution appears to poison the catalyst.[140] Watt, Barnett and Vaska[141] have also studied the catalyzed reaction between sodium and liquid ammonia. The reaction is catalyzed by metals in general and most effectively by those of the transitional series. It is unfortunate that some of the most effective catalysts are the metals most commonly used as materials of construction. Rate measurements have been made by collecting the hydrogen evolved during the catalyzed reaction and the following results are expressed as (c.c.H_2/h./g.Na/sq.mm. catalyst area) × 10^2: tantalum, 0·24; monel, 1·0; stainless steel (Carpenter 20), 5·1.

The following value has been given for the heat of formation of sodamide:

$Na(c) + 0{\cdot}5N_2(g) + H_2(g) = NaNH_2(c) + 27$ kg.-cal.[138,142]

Dry sulphur dioxide does not react with sodium at room temperature but the moist gas reacts almost as vigorously as water though without luminescence.[2] Only a partial dulling of the surface of sodium is observed after storage in liquid sulphur dioxide for several months.[143] Liquid sodium reacts with sulphur dioxide to give sodium sulphide and sulphate: $4Na + 2SO_2 \rightarrow Na_2S + Na_2SO_4 + 18{\cdot}24$ kg.-cal.[33]

It is believed that alkali metal hyposulphites have not been prepared successfully by the direct action of sulphur dioxide on sodium. When, however, the alkali metal is in the form of an addition product with certain ethers, the hyposulphite can be obtained in good yield by the action of sulphur dioxide. An example is given: 100 parts of a dispersion of sodium in xylene (50%Na) are added to a reaction vessel containing ethylene glycol dimethyl ether. The mixture is stirred and sulphur dioxide continuously passed at a temperature of 10° C. When the reaction subsides the stirring and passage of sulphur dioxide are stopped and the sodium hyposulphite, which is in the form of a white precipitate, is separated by means of a centrifuge, washed with alcohol and ether and dried. Other ethers of polyhydric alcohols which may be used are listed. Sodium hyposulphite is also formed when sulphur dioxide is allowed to react with sodium-naphthalene or sodium-benzophenone addition compounds in ethylene glycol diethyl ether but is contaminated with naphthalene and benzophenone.[144]

The manufacture of sodium dithionite (hydrosulphite, hyposulphite, $Na_2S_2O_4$) from sulphur dioxide and sodium amalgam is described by Dijs, Hoogland and Watermann.[145] Sodium amalgam is passed by a centrifugal pump at the rate of 1 l./min. from an electrolyzer to the top of a reactor where it divides into droplets and comes in contact with a buffer solution made up of a 5% solution of sodium bisulphite–sodium sulphite of pH 5–5·5. As soon as the circulation of the solution and amalgam is started, sulphur dioxide is passed into the reactor at a rate which maintains the desired pH value. With a buffer solution of pH less than 5 low yields are obtained; at pH values greater than 5·5 hydrogen sulphide is obtained as one of the reaction products. The temperature must be less than 40° C. By feeding buffer solution into the reactor and drawing off an equal volume of sodium dithionite solution, the process becomes entirely continuous. The denuded amalgam falls to the bottom of the reactor and is returned by gravity flow to the electrolyzer. The process can be automatically controlled. Sodium sulphide is used to precipitate small amounts of dissolved mercury in the form of the sulphide, HgS, which may be removed by filtration. A 15% solution of the dithionite can be obtained with a yield of 80–90% calculated on the current consumption, and a yield of 90% based on sodium amalgam used. The procedure and apparatus used for the continuous production of an aqueous solution of sodium dithionite from sodium amalgam and sulphur dioxide have also been described.[146] The reactions occurring are: $2Na_2SO_3 + 2H_2O + 2SO_2 \rightarrow 4NaHSO_3$ and $4NaHSO_3 + 2Na \rightarrow Na_2S_2O_4 + 2Na_2SO_3 + 2H_2O$. The temperature should be 10°–25°C., preferably above 15°C., and the pH of the solution 5·4–5·8. The dithionite solution should remain in the reactor as short a time as possible to prevent the formation of thiosulphate, and the solution should be as concentrated as possible in order to effect separation by addition of sodium chloride. In this process two reactors are used, the buffer solution reacting separately with sulphur dioxide and the amalgam respectively. An equally intensive circulation is necessary between the two reactors. After treatment with sulphur dioxide the solution is cooled before treatment with sodium amalgam. The concentration of the amalgam is preferably 0·01–0·05% and it is important that the amalgam should be discharged before it is completely denuded, *i.e.* when the concentration has fallen to 0·001–0·002%. With a buffer solution of sulphite–bisulphite with concentrations of sulphur dioxide up to 70g./l. and with an introduction of gaseous sulphur dioxide in stoicheiometric ratio with the sodium as amalgam it is possible to obtain solutions of dithionite to the solubility limit capable of giving a solid product with a titre over 85%$Na_2S_2O_4$ and yields between 50% and 65%. From buffer solutions containing at least 15g./l. of sulphur dioxide, yields of 70–80% of dithionite solutions containing 40g./l. $Na_2S_2O_4$ can be obtained. There are numerous other references to the reaction of sulphur dioxide with sodium amalgam.[28,30,147-153]

Aqueous sodium thiosulphate solutions are reduced with sodium amalgam to yield equimolecular proportions of sulphide and sulphite ions. It is assumed that reduction is brought about by sodium atoms rather than by an electrical charge removal since the S_2O_3 ion is not reduced at the dropping-mercury electrode for voltages up to −2·5V. (against saturated calomel) whereas the potential with sodium amalgam is about −2·15V.[154]

The reaction of sodium vapour with sulphur dioxide and trioxide at 238°C. and at low pressures has been studied by Bawn and Evans by the diffusion flame method already described (see page 442). Both of these gases show remarkable reactivity towards sodium atoms, reaction occurring at about one collision in ten. The mechanism of the reaction is given by the following equations where X represents sulphur dioxide or trioxide: $Na + X \rightarrow NaX^*$; $NaX^* \rightarrow Na + X$; $NaX^* + N_2 \rightarrow NaX + N_2$. Nitrogen acts as a third body, carrying away the energy of the reaction. The results are given in Table V.[41]

TABLE V. - REACTION OF SODIUM VAPOUR WITH SULPHUR DIOXIDE AND SULPHUR TRIOXIDE AT 238°C.

Reaction partner	Pressure of Na at nozzle mouth mm. × 10^3	Rate of flow of N_2 mol./sec. 10^8	Rate of flow of reaction partner mol./sec. 10^8	Total pressure in reaction vessel mm.	Partial pressure of reaction partner mm.	Diffusion coefficient of Na mol./cm.^{2}/sec.	Radius of flame cm.	Velocity constant c.c.mol.$^{-1}$sec.$^{-1}$
SO_2	3·104	1401	0·806	3·66	0·021	130·4	1·52	$1{\cdot}69 \times 10^{13}$
SO_2	3·104	1437	0·974	3·69	0·024	129·3	1·60	$1{\cdot}25 \times 10^{13}$
SO_3	3·954	1237	1·243	3·38	0·034	141·3	1·10	$2{\cdot}28 \times 10^{13}$

The rate of reaction of sodium atoms with sulphur hexafluoride has been measured by the diffusion flame method. A thick film of sodium is deposited *in vacuo* on the side of a Pyrex tube and sulphur hexafluoride introduced at a pressure up to 10mm.Hg. At room temperature no reaction occurs but at 200–300°C. the pressure falls to less than 0·1mm. in eight minutes and the sodium surface is covered with a brown incrustation. With sulphur hexafluoride at 235·5mm. and at 300°C. the reaction stops after only 10mm. of gas is absorbed. At 500°C. the reaction is accompanied by luminescence of the sodium *D*-line. The gas-phase reaction: $SF_6 + Na \rightarrow SF_5 + Na^+F^-$, is exothermic, about 37 kg.-cal. being evolved; with a sodium surface the reaction would be even more exothermic. The chemiluminescence is probably caused by one of the five stages of the reaction: $SF_n + Na \rightarrow SF_{n-1} + Na^+F^-$ ($n \leq 5$) which is exothermic to a greater extent than 49 kg.-cal., the energy required to excite the *D*-line. The bimolecular velocity constant at 247° C. is $2{\cdot}23 \times 10^{13}$c.c. per mole per sec.[155]

Sodium begins to react with the vapour of thionyl chloride at 100° C., the surface of the sodium becoming covered with a protective film of sodium chloride which prevents further action. At 300° C. a considerable amount of sulphur monoxide is formed and the reaction proceeds with the production of a flame: $SOCl_2 + 2Na \rightarrow 2NaCl + SO$.[156]

According to Hubbard and Luder the reaction with boiling thionyl chloride is very slow.[157]

Diethyl sulphite, $SO(OC_2H_5)_2$, does not react with sodium at 300° C. and the metal may be distilled unchanged.[156]

The atomic reactions of sodium and sulphur mono- and di-chloride at 270° C. have been studied by the diffusion flame method, the partial pressure of the sodium being about 3×10^{-3}mm.Hg and that of the inert carrier gas, nitrogen, 1–10 mm.Hg. The reaction with the dichloride is almost instantaneous, reaction occurring at practically every collision. The velocity constant is 6340c.c.$mole^{-1}sec.^{-1} \times 10^{-11}$. The reaction with the monochloride is slower, the collision number being about 3·6 and the velocity constant 1760 c.c.$mole^{-1}sec.^{-1} \times 10^{-11}$. Both reactions are accompanied by a blue luminescence but the light intensity is greater with the dichloride.[158]

A mixture of sodium and sulphur dichloride explodes when hit with a hammer.[112]

When solid sulphides of the non-noble metals, with the exception of magnesium, are intimately mixed with alkali metal amalgams in the presence of sufficient water for reaction (with the exclusion of air or in a protective atmosphere and at an elevated temperature) the non-noble metals are precipitated quantitatively and in powdered form. Alkali metal sulphides are formed. The reaction may be conducted in the molten state or in the gaseous phase, preferably in a closed cycle and continuously.[159]

Nitrogen does not appear to react with sodium and is in fact recommended for blanketing liquid sodium during handling.[9] A method, probably originating with Bunsen in the Heidelberg laboratory, for obtaining lustrous sodium by filtering in nitrogen is described by Bornemann.[160] A clean, dry glass tube about 15–20 mm. wide is sealed at one end and a constriction of diameter 3–4 mm. is made at about 20cm. from the bottom. A clean metal sieve (1mm. mesh) is placed at the constriction so as to press tightly against the sides of the tube, and freshly cut sodium is placed on the sieve and the tube sealed off at about 20cm. above the constriction. The metal forms oxide which absorbs carbon dioxide in the air leaving only nitrogen in the tube. After some hours the metal is carefully melted, with the tube in a horizontal position to prevent the molten metal passing the sieve, and if on cooling and standing for some time the metal remains lustrous, the tube is placed in a vertical position and heated at first from the sieve down to the constriction and later up to the metal. The metal flows through the sieve but the carbonate, hydroxide or oxide does not. The tube is finally sealed off at the constriction.

Guernsey and Sherman[161] have shown that when nitrogen heated to 1000° C. is passed over sodium at 800° C., neither sodium nitride nor azide is formed. Iron has no catalytic effect.

The reaction between strontium and nitrogen to form strontium nitride is accelerated by sodium.[162] Sodium acts as an 'exciter' in the calcium/nitrogen reaction and after the reaction is started it proceeds more rapidly if the sodium is removed from the surface of the calcium.[163] Nitrogen is removed from argon by treatment with calcium activated with sodium. Calcium activated in this way reacts a hundred times faster with nitrogen than does untreated calcium. Spectroscopically pure argon is easily prepared in this way.[164]

Fischer and Schröter[165] state that sodium nitride, contaminated with a fine metallic dust mostly black in colour, is formed when an electric discharge is passed between sodium electrodes through a liquid mixture of 90% argon and 10% nitrogen. This contaminated sodium nitride is considered by Moldenhauer and Mottig[166] to be a mixture of sodium azide and sodium.

Wattenberg[167] has subjected nitrogen, at a pressure of 1–10mm. Hg, to the action of an electric discharge in the presence of finely divided sodium and obtained the results given in Table VI.

TABLE VI. - REACTION BETWEEN SODIUM AND ACTIVATED NITROGEN

Time min.	c.c. N_2 at 0°C. and 760mm.	Reaction product	
		% Nitride	% Azide
1	0·5	100	-
5	0·9	100	-
110	1·6	54	46
264	4·1	27	63

Sodium nitride and activated nitrogen have been shown to give sodium azide.

The literature on the stability, thermodynamics and photochemistry of the metallic salts of hydrazoic acid has been reviewed by Racz;[168] the equilibrium constants calculated for the possible formation of the sodium derivatives are shown in Table VII.

TABLE VII. - EQUILIBRIUM CONSTANTS FOR THE REACTIONS:

(*a*) $3Na + 0{\cdot}5N_2 = NNa_3$;
(*b*) $Na + 1{\cdot}5N_2 = N_3Na$, and
(*c*) $N_3Na + 2Na = NNa_3 + N_2$.

Temperature °K.	Log *Kp*		
	(*a*)	(*b*)	(*c*)
300	-18·9	-19·3	+0·4
400	-19·6	-18·9	-0·7
500	-20	-18·8	-1·4
750	-21	-18·8	-2·5
1000	-22	-18·9	-3·2

According to Kichlu, sodium is ionized when acted upon by active nitrogen.[169] The transfer of energy between active nitrogen and sodium has also been described: active nitrogen, liberated by thermal decomposition of silver azide, excites ultra-violet fluorescence in certain metallic vapours and, under vacuum at 272°C. and in the presence of sodium (0·01mm.), the emission is four times as intense as with silver azide alone.[170]

In the presence of carbon and metal oxides, sodium reacts with nitrogen to form sodium cyanide.[33]

Sodium and phosphorus, when heated together in the atomic ratio of 3:1 in an argon atmosphere in a corundum crucible enclosed in a gas-tight iron container, yield a homogeneous product, Na_3P, which is extremely sensitive to air. This compound does not appear to be formed when the elements are brought together in liquid ammonia.[171]

The conditions for the preparation of the compound, Na_2P_5, described by Hackspill and Bossuet[172] have been found by studying the thermal dissociation of sodium dihydrogen phosphide, NaH_2P. Below 100°C., this compound dissociates giving a yellow amorphous powder of disodium hydrogen phosphide and liberating pure hydrogen phosphide: $2NaH_2P \rightarrow Na_2HP + PH_3$; the dissociation pressure of disodium hydrogen phosphide is inappreciable up to 100°C., but the proportion of phosphine in the gas evolved between 100° and 150°C. decreases and the amount of hydrogen increases owing to the reaction: $Na_2HP \rightarrow 2Na + P + 0{\cdot}5H_2$. At 380°C. the vapour pressure of sodium is sufficiently high for some distillation to occur, and by very careful distillation over a period of 150 hours at 450°C. a yellow product, Na_2P_5, is obtained: $5Na_2HP \rightarrow Na_2P_5 + 8Na + 2{\cdot}5H_2$.[173]

Sodium reacts with phosphorus in the presence of air to form sodium phosphate.[33]

A brown-violet powder of composition Na_3As is obtained when sodium vapour is passed over heated arsenic in a hard glass tube which has been previously evacuated.[171] No indication of compound formation is given by potentiometric titrations of elementary arsenic in liquid ammonia solutions of sodium, but when liquid ammonia solutions of arsenic trisulphide are used the following compounds are shown to exist: Na_3As, Na_3As_3, Na_3As_5 and Na_3As_7[123] (see also page 511).

Arsenic and arsine are formed when arsenic trioxide in an aqueous buffered solution is reduced with sodium amalgam (0·6%Na). At pH 8·5 the fraction of reduced arsenic appearing as the metal varies from 13·2 to 1·3% as the initial concentration of As(III) varies from 0·1 to 0·01mole/l. The formation of arsenic is favoured by increase of temperature. The fraction reduced to arsenic with a solution of 0·051mole/l. As(III) increases from 11·5 to 68·2% as the pH is increased from 8·5 to 14·3. In the presence of excess of sodium amalgam arsenic is first formed and then reduced to arsine with hydrogen formed by reaction of sodium with water.[174]

Sodium thioarsenate solutions are reduced by sodium amalgam to yellow arsenic which forms as a precipitate and is soluble in and may be crystallized from carbon disulphide. This form of arsenic is converted by light into ordinary arsenic.[175]

A bluish-gray compound with a metallic lustre, Na_3Sb, is formed when sodium and antimony are heated together in an atmosphere of argon in the atomic ratio of 3:1 at a temperature about 50° to 100° above the melting point. The reaction may be carried out in a stoppered iron crucible.[171] For reactions in liquid ammonia, see page 512.

Sodium hydroxide solutions of antimony oxide, Sb_2O_3, buffered at pH 8·53, are reduced by 0·5% sodium amalgam and yield less stibine, SbH_3, more antimony and more trivalent ion, Sb^{+++}, in solution in thirty minutes than the corresponding products from arsenic trioxide solutions. The absolute yield of stibine is practically constant for Sb(III) concentrations above 2%; the antimony yield is greater than the sum of stibine and dissolved ion, Sb^{+++}, and both the antimony and ion yields increase with Sb(III) concentration. The stibine fraction increases with decreasing Sb(III) concentration but is less when nitrogen is used as carrier gas than when carbon dioxide is used; it is also less at 60° than at 20°C. and after 30 minutes rather than 60 minutes.[176]

A mixture of sodium and phosphorus pentachloride or tribromide explodes violently when struck with a hammer.[112]

The reactions between phosphorus trichloride, phosphorus oxychloride, arsenic trichloride and sodium vapour at 270°C. and about 3×10^{-3}mm., in the presence of an inert carrier gas such as nitrogen at 1–10mm. pressure, have been studied by Heller and Polanyi.[158] Phosphorus oxychloride reacts more readily than phosphorus trichloride, which reacts at about the same rate as arsenic trichloride. The reaction velocity constants expressed as c.c.mole^{-1} sec.$^{-1}$ × 10^{11} are: 2290($POCl_3$), 1500(PCl_3), 1470($AsCl_3$). The first two reactions are accompanied by luminescence, the oxychloride reaction emitting a bluish-grey light, and the phosphorus trichloride reaction emitting the *D*-line of sodium. No luminescence is observed with arsenic trichloride.

Nitrous oxide reacts with sodium to form sodium oxide and nitrogen: $2Na + N_2O \rightarrow Na_2O + N_2$; $\Delta H^\circ_{298} = -118·89$; $\Delta F^\circ_{298} = -114·76$ kg.-cal./mole.[33]

The diffusion flame technique has been used by Bawn and Evans[41,177,178] to study the rates of reaction of sodium vapour at low pressures with oxides of nitrogen at about 260°C. The reactions with nitrous oxide and nitrogen peroxide are accompanied by a marked luminescence, that with the former being the much more intense; with nitrous oxide, reaction occurs at about one collision in forty and with nitrogen peroxide at about one in ten. Experimental details and results for these two oxides are given in Table VIII.

TABLE VIII - REACTIONS OF SODIUM VAPOUR WITH NITROUS OXIDE AND NITROGEN PEROXIDE

Reaction partner	Pressure of Na at nozzle mouth mm. × 10^3	Temp. of reaction zone °C.	Streaming velocity of carrier gas mol./sec. × 10^8	Rate of flow of reaction partner mol./sec. × 10^8	Total pressure in reaction vessel mm.	Partial pressure of reaction partner mm.	Diffusion coefficient of Na mol./cm.^{2}/sec.	Radius of flame cm.	Velocity constant c.c.mole^{-1}sec.$^{-1}$ × 10^{-12}	Collision number	Activation energy g.-cal.
N_2O	10·6	262	1600	5·2	3·82	0·0123	134	1·34	9·8	40	3900
	7·5	253	1100	3·2	3·65	0·0102	137	1·40	9·8	40	3900
	107·9	275	1500	4·4	3·83	0·0109	128	1·43	16·8	24	3500
	3·2	262	1600	4·4	3·95	0·0110	129	1·25	8·4	50	4200
	3·6	260	1300	4·0	3·69	0·0110	138	1·11	11·6	36	3800
	3·7	260	1400	4·0	3·65	0·0109	139	1·03	14·1	29	3600
NO_2	2·5	252	1100	1·0	3·12	0·0030	160	0·95	58·1	7	2000
	2·2	253	1100	1·0	3·19	0·0030	156	1·12	40·2	10	2400
	2·1	249	1100	1·0	3·26	0·0030	151	1·02	45·6	9	2300
	2·4	253	1600	1·7	3·87	0·0041	129	0·97	32·6	12	2600
	2·2	254	1600	1·7	3·87	0·0041	129	1·38	15·4	16	2900

The following mechanism is postulated: $Na + N_2O \rightarrow NaC + N_2$; $NaO + Na_2 \rightarrow Na_2O^* + Na$; $Na_2O^* + Na \rightarrow Na_2O + Na^*$; $Na^* \rightarrow Na + h\nu$.[178]

The reaction of sodium vapour with nitric oxide has been studied by the foregoing method and also by a modified streaming method permitting higher inert gas pressures to be used. The results for the streaming method, given in Table IX, are considered to be the more accurate.

TABLE IX. - REACTION OF SODIUM VAPOUR WITH NITRIC OXIDE AT 260°C.

Reaction partner	Pressure of Na at nozzle mouth mm. × 10^3	Rate of flow of N_2 mol./sec. × 10^8	Rate of flow of NO mol./sec. × 10^8	Total pressure in reaction vessel mm.	Partial pressure of NO mm.	Diffusion coefficient of sodium mol./cm.^{2}/sec.	Radius of flame cm.	Velocity constant c.c.mol.$^{-1}$sec.$^{-1}$ × 10^{10}
NO	1·64	3311	682·3	5·17	0·884	98·24	1·75	1·45
	1·64	3299	80·3	10·00	0·238	50·81	1·75	2·78
	1·64	3370	70·6	11·67	0·239	43·56	1·75	2·37
	1·64	3158	36·12	15·14	0·171	33·58	1·75	2·55
	1·64	3192	15·36	20·00	0·096	25·41	1·75	3·45
	1·64	3335	9·64	23·80	0·069	21·35	1·75	4·05
	1·64	3333	5·09	32·00	0·044	15·89	1·75	4·69
	1·64	3335	3·12	37·4	0·035	13·58	1·75	5·07
	1·64	3378	1·84	44·6	0·024	11·39	1·75	6·10
	1·64	3294	1·43	50·2	0·022	10·12	1·75	6·05

The reaction occurs according to the following mechanism: $Na + NO \rightarrow NaNO^*$; $NaNO^* \rightarrow Na + NO$; $NaNO^* + N_2 \rightarrow NaNO + N_2$. A termolecular reaction occurs at low inert gas pressures; the unstable associated molecule, $NaNO^*$, which has a lifetime of about 10^{-9} seconds, dissociates or is stabilized by subsequent collision with a nitrogen molecule. At higher inert gas pressures, the reaction changes over to a simple bimolecular mechanism.[41]

When shaken with sodium amalgam, nitric oxide reacts to form the compound, NaNO, which is found by X-ray diffraction to be identical with the compound formed when nitric oxide reacts with sodium in liquid ammonia but different from sodium hyponitrite. The compound is obtained in quantitative yield.[179]

When sodium is heated in nitrogen containing about 20% of nitric oxide, the metal becomes bluish-green at about 60° to 70°C. and reaction sets in at about 160° to 170°C. The solid yellow product dissolves in ice-cold water to give an alkaline solution of sodium nitrite and hyponitrite, $Na_2N_2O_2$, and nitrous oxide is evolved.[180]

A mixture of sodium nitrite and nitrate is produced when sodium is burnt in gaseous dinitrogen tetroxide.[13] At the temperature of burning sodium, the gaseous phase contains oxygen and nitric oxide which give rise to the nitrite. Crystallographic analysis of the reaction products formed when liquid dinitrogen tetroxide is treated with sodium show the white solid product to be crystals of sodium nitrate. A marked increase in the speed of the reaction occurs when a potential difference is applied while the reaction is taking place.[181] The reaction of metallic sodium with a gaseous mixture of N_2O_4-NO_2 molecules has been studied by passing the gas mixture over the metal at 60° to 80° C. and at atmospheric pressure. A thin coating of a white solid is acquired in about 15 minutes and then becomes sufficiently cohesive to prevent further action. An *X*-ray powder photograph of the product is identical with that of pure sodium nitrite.[182]

Nitrogen peroxide is liberated and a white crystalline solid identified as sodium nitrate is formed when small pieces of sodium are added to liquid nitrogen pentoxide at -40° C.[181]

Sodium reacts with sodium nitrite in liquid ammonia to form a bright yellow precipitate of disodium nitrite, Na_2NO_2. This compound is also formed when a solution of sodium nitrite in liquid ammonia is electrolyzed, and is seen as a bright yellow deposit on the cathode[183,184] (see also page 518).

The rates of reaction of sodium atoms with nitromethane, ethyl nitrate and amyl nitrite have been measured by the diffusion flame method, with the results given in Table X.[178]

Neither graphite nor diamond appears to react with sodium at any temperature, and dry graphite powder can in fact be used to smother sodium fires.[33,143,185,186] Herold[187] states that sodium does not react with graphite even at 500° C. Blue or black products, poor in alkali metal, obtained by operating at 900° C. in mild steel, suggested that sodium does in fact form compounds with carbon analogous to those of the other alkali metals but much less stable.

Recently evidence has been obtained for the existence of a lamellar compound of sodium with graphite of composition $C_{60}Na$-$C_{68}Na$, probably $C_{64}Na$. The compound is very similar to the parent graphite, but has a deep violet tinge. It is prepared by heating powdered graphite with about 3% of sodium of commercial purity, filtered through sintered glass at about 150° C. The reaction is carried out in a helium atmosphere containing less than 20p.p.m. of oxygen in a 'glove box', with stirring for one hour at about 400° C. The experimental conditions are not critical. The most sharply defined *X*-ray diffraction pattern is obtained when the product is made from highly crystalline, *i.e.* purified, natural graphite, and definition is also improved by prolonged heating at 400° C. The sodium atoms appear to lie in interstitial planes separated by eight carbon layers. At every eighth layer the spacing is increased from 3·35A. to 4·6A., which is consistent with the atomic diameters of sodium and carbon.[188]

Sodium wets graphite above 450° C. and when a graphite rod is immersed in the molten metal in a helium atmosphere, with about 6in. of the rod above the surface, about 60% of the voids in the graphite are filled with sodium, presumably by capillary action. At 550° C. and after 50 hours, all the voids are filled. Since sodium has a relatively high thermal conductivity, hot graphite immersed in cooler sodium may be fractured by thermal shock. In circulating non-isothermal systems where sodium is in contact with graphite, there is a mass transfer of carbon from the hot regions and a deposition in the colder regions. In static systems liquid sodium corrodes graphite at insignificant rates unless a 'sink' is available to remove the carbon that enters the sodium. Stainless steel at temperatures above 500° C. acts as a 'sink'. No quantita-

TABLE X.- REACTION OF SODIUM WITH NITROMETHANE, ETHYL NITRATE AND AMYL NITRITE

Reaction partner	Pressure of Na at nozzle mouth mm. × 10^3	Temp. of reaction zone °C.	Streaming velocity of carrier gas mol./sec. × 10^8	Rate of flow of reaction partner mol./sec. × 10^8	Total pressure in reaction vessel mm.	Partial pressure of reaction partner mm.	Diffusion coefficient of Na mol./cm.^{2}/sec.	Radius of flame cm.	Velocity constant c.c.mole^{-1}sec.$^{-1}$ × 10^{-12}	Collision number	Activation energy g.-cal.
CH_3NO_2	2·0	255	1300	0·8	3·45	0·0021	145	1·12	51·7	8	2200
	2·0	255	1200	0·8	3·49	0·0021	143	1·29	38·2	11	2500
	2·0	255	1100	0 0·7	3·26	0·0021	154	1·29	41·0	10	2400
	2·3	255	1200	0·6	3·26	0·0017	154	1·31	52·8	8	2100
$C_2H_5NO_3$	2·0	254	1100	0·5	3·28	0·0015	152	1·53	39·8	10	2400
	1·9	253	1300	0·5	3·49	0·0013	143	1·52	43·8	9	2300
$C_5H_{11}ONO$	1·6	249	1900	1·2	4·16	0·0027	118	0·94	42·1	10	2400
	2·0	253	1800	1·2	4·06	0·0027	123	1·4	21·5	18	3100

The measured velocity constants refer to the primary reaction: R.N=O + Na R-N- + NaO. The high collision yields are about 1 in 10.[178]

tive data are available for the solubility of carbon in sodium.[33] The literature on the reactions of sodium with graphite has been reviewed by Monet.[189]

Other forms of carbon such as soot or lampblack are attacked by sodium at elevated temperatures, and Table XI gives the amount of shortening which occurs when small sticks of retort carbon are heated for 1·5min. in sodium vapour at various temperatures. Probably a solid solution of the alkali metal in carbon is formed. Carbon powder accumulating on the surface of the evaporating metal in contact with air sometimes ignites with violent explosions.[190]

Petroleum coke, lampblack and metallurgical coke, passing a 200 mesh

TABLE XL - SHORTENING OF CARBON RODS HEATED IN SODIUM VAPOUR

Temp. °C.	Shortening, cm.
400–500	No change
520–575	Very little change
575–675	0·2
740–825	0·6
840–915	1·0

sieve, have been heated with sodium at 900°C. in an evacuated Monel tube closed at its cooled end with a plug of sodium in order that the pressure of sodium vapour can be built up. Petroleum coke and lampblack yield considerable quantities of sodium carbide, but no carbide can be detected when metallurgical coke is used. The reaction is not catalyzed by iron.[161]

Sodium and potassium residues in large amounts can be disposed of by burning in an open fire of charcoal or coke stirred with an iron rod. On cooling, the residue, largely sodium carbonate, can be thrown into large containers of water.[143]

The reactions of the steam–carbon system have been studied by a static method at 750°C. with extracted coconut charcoal to which various catalysts have been added. Sodium catalyzes this reaction and also the carbon dioxide reaction. The oxidation of carbon monoxide by steam is also enhanced by sodium.[191]

The formation of sodium carbonyl directly from sodium and carbon monoxide has not been reported.[33] A lilac coloured solid, NaCO, is, however, formed when carbon monoxide is led into a liquid ammonia solution of sodium at -50°C. It decomposes at 90°C.: $4NaCO \rightarrow Na_2CO_3 + Na_2O + 3C$. When heated in air, sodium carbonyl explodes.[143]

Sodium can be made to react with carbon monoxide to form sodium carbide and carbonate: $4Na + 3CO \rightarrow Na_2C_2 + Na_2CO_3$; the reaction is endothermic and the highest yield of carbide is obtained when the reaction temperature is in the range 625–780°C. Under optimum conditions the product is substantially white, but in some cases it may be grey or black owing to a certain amount of decomposition of carbon monoxide to carbon. The sodium is contained in small steel containers made to withstand pressure and carbon monoxide is led in while the containers are shaken in an electric furnace at 625° to 780°C. The product is somewhat fluid at the reaction temperature but sets to a hard, dense material on the cooled surface of the apparatus. The product contains 20 to 39·76wt.-% of sodium carbide, the rest being largely sodium carbonate with minor amounts of sodium or sodium monoxide and traces of sodium cyanide. A more economic process is to use the old Deville process to obtain sodium from sodium carbonate and to allow the sodium vapour and carbon monoxide to react together: $2Na_2CO_3 + 4C \rightarrow 4Na + 6CO$; $4Na + 3CO \rightarrow Na_2CO_3 + Na_2C_2$. The reaction: $2CO \rightleftharpoons CO_2 + C$, also occurs to some extent. Sodium carbonate and finely divided petroleum coke are heated together at 1050° to 1200°C. and the sodium vapour and carbon monoxide formed in the reaction are cooled to 625° to 780°C. by bringing the gas mixture into contact with a mass of steel bodies, each having a mass equal to that of a steel sphere of 0·2 to 2in. in diameter. The condensed material is in the form of a pasty solid, and on cooling to room temperature a hard, dense, enamel-like product is obtained which is very difficult to remove. The product may by treated *in situ* with water to give acetylene.[192]

Sodium vapour, carbon monoxide and nitrogen when passed through a 60-watt lamp, operating at its normal temperature, react to form sodium cyanide: $3Na + CO + N \rightarrow NaCN + Na_2O$. About 0·5g. of sodium cyanide is formed in 100 hours.[193]

The slow oxidation of carbon monoxide by nitrous oxide is catalyzed by performing the reaction in vessels coated with sodium chloride or bromide. Simultaneous emission of the sodium resonance lines is also observed and the following reactions have been suggested, although the mechanism of the formation of sodium atoms from the halides is uncertain: $Na + N_2O \rightarrow NaO + N_2$; $NaO + CO \rightarrow Na^* + CO_2$; $Na^* \rightarrow Na + h\nu$. This mechanism is confirmed as follows. Sodium vapour at 300° C. is led into a reaction chamber containing nitrous oxide at 350° to 375°C. and the products are condensed and analyzed for carbon dioxide and nitrous oxide: the results obtained in 1 to 1·5 hours using nitrogen as carrier gas at a velocity of $1{\cdot}7 \times 10^5$ mole/sec. are given in Table XII.

TABLE XII. - REACTION OF SODIUM VAPOUR WITH CARBON MONOXIDE AND NITROUS OXIDE AT 350° TO 375°C.

Temp. °C.	pNa mm.	pN_2 mm.	pCO mm.	pN_2O mm.	Condensate		Yield CO_2/Na	Yield /N_2O
					CO_2%	N_2O%		
375	0	4·4	2·2	0·88	0	98	(Sodium omitted)	
350	0·014	7·8	0	0·77	0	96	-	-
350	0·014	6·0	3·0	0	No condensate		-	-
350	0·014	5·16	2·57	0·77	43	57	24	31
350	0·014	4·17	1·33	0·83	40	60	24	29
350	0·014	2·54	1·27	0·19	33	65	4·5	24
375	0·014	4·29	2·14	1·07	42	59	32	30

The slow nitrous oxide/carbon monoxide reaction does not excite the metal lines when the vessels are coated with potassium chloride or sodium iodide but the red lithium lines are briefly excited when the coating is lithium chloride.[194]

The reactions of metal carbonyls with sodium in liquid ammonia solutions are referred to elsewhere (see page 519).

The carbonyl $[Co(CO)_4]_2$ reacts with sodium amalgam to give the sodium salt; $Na[Co(CO)_4]$.[195]

An explosive reaction occurs when sodium and solid carbon dioxide are brought together by impact.[143,196-198] At room temperature there is apparently no reaction between sodium and carbon dioxide,[2,143] but at red heat free carbon, sodium monoxide and sodium carbonate are formed.[143] It would appear from the following experiment that although sodium burning freely in air burns with increased vigour when the air is replaced by carbon dioxide, the gas can be used to extinguish solvent-fires in their initial stages even when sodium is present. Acetone was poured into a metal tray and sliced sodium was distributed on the tray. On ignition the solvent burned while the sodium melted without burning. When the maximum temperature was apparently reached, carbon dioxide was applied and the solvent fire was extinguished without ignition of the sodium. The sodium appears to be protected by a blanket of solvent vapour from the intense heat required for its ignition.[199]

According to Haupt[200] sodium is converted quantitatively into sodium oxalate by injecting molten sodium at 150° to 200°C. and carbon dioxide at 360° to 400°C. and at 0·5atm. into a sheet iron chamber. The carbon dioxide is present in excess and unchanged gas escapes through a vent and is recycled. The sodium oxalate formed falls to the bottom of the chamber: $2Na + 2CO_2 \rightarrow Na_2C_2O_4$. The sodium is melted under a mineral oil or in a nitrogen atmosphere. Reactions between carbonyl compounds and amalgams have been studied by Henglein and Sontheimer.[201] The conversion of carbon dioxide and sodium amalgam to sodium oxalate is about 80% complete at room temperature and decreases with increasing temperature. A relation between yield and half-wave potential of the amalgam is indicated by the following data.

Amalgam	Half-wave potential	Yield % at t°C. 20°	100°	200°	225°	250°
Zn	−1·06V.	–	No reaction			
Mn	−1·55	–	Practically no reaction			
Na	−2·15	75	55	47	–	41
K	−2·17	25	60	72	68	61
Ca	−2·23	4	–	–	–	–
Li	−2·31	0·1	–	–	–	4·5

Hohn, Fitzer and Nedwed[202] report that pure carbon dioxide and sodium amalgam give a 100% conversion to oxalate. With 0·02–0·2% sodium amalgam the reaction velocity is practically independent of concentration; the conversion rate is increased by stirring although the total yield is unchanged; the reaction rate seems to increase with decreasing temperature. Water vapour present in the carbon dioxide causes the formation of sodium carbonate or bicarbonate or both these salts as well as some carbon monoxide; oxygen gives some peroxide while hydrogen and nitrogen do not affect the net result. An example given in a patent[27] states that the amalgam is violently agitated during the process so that the amalgam surface is continuously destroyed; sodium oxalate containing 0·3% of sodium carbonate is produced from sodium amalgam and dry carbon dioxide. Thermodynamic calculations indicate that the amalgams of sodium, potassium, lithium, calcium, barium, manganese and zinc should react with carbon dioxide to give oxalates, whereas those of cadmium and copper should not. Only the amalgams of lithium, calcium, barium, manganese and zinc should reduce carbon dioxide to carbon monoxide. The effects of sodium concentration and of temperature change have been reported[202] but the effect of motion of the amalgam is greater than had been supposed. The reaction rate increases linearly with increase of carbon dioxide pressure. If the sodium content is greater than 0·007% and the carbon dioxide pressure greater than one atmosphere, the regeneration of the surface of the amalgam determines the rate and not a diffusion process. The amount of oxalate formed decreases as the amount of air added is increased and with 50% of air no oxalate is formed[203] (see also [204,205]).

An amalgam containing 0·1% of sodium is placed in a gas-tight chamber in which brushes or scrapers are rotated at high speed, e.g. 1000 r.p.m. in contact with the walls of the vessel. The amalgam surface, rapidly and continuously disrupted in this way, is allowed to react with dry carbon dioxide at 20°C. to give an almost 100% yield of sodium oxalate with about 0·3% of sodium carbonate. At the completion of the test freshly boiled distilled water is added with stirring and without entry of air. The aqueous sodium oxalate and mercury separate smoothly into distinct layers.[29]

An account of the technical and economic aspects of the use of sodium amalgams for the production of sodium compounds including sodium oxalate is given by Nicolai.[30] Sodium amalgam reacts with carbon dioxide in aqueous solution to form sodium formate and sodium hydroxide: $2Na + CO_2 + H_2O \rightarrow HCOONa + NaOH$.[30]

Atomic reactions of sodium with carbon dioxide have been studied at 260° C. in the presence of an inert carrier gas such as nitrogen at a pressure of 3 to 13mm. Hg. No reaction occurs.[41]

Finely dispersed sodium, produced during the electrolysis of aluminium oxide dissolved in cryolite using carbon electrodes, may reduce carbon dioxide, formed by the action of oxygen on the carbon anode, to carbon monoxide.[206]

An abrasive crystalline carbon is said to be produced by the action of sodium on carbon dioxide or carbon monoxide at 50–100atm. pressure and 1000° to 1500° C.[207]

The reaction of sodium atoms with phosgene has been studied by the diffusion flame method. At a temperature of 270° C., using a partial pressure of sodium vapour about 3×10^{-3}mm., and a partial pressure of the inert gas about 1 to 10mm., the reaction velocity constant is 856c.c.mole^{-1}sec.$^{-1}$ $\times 10^{-11}$ and the collision number 7. The luminescence which accompanies the reaction is due to the excitation of the *D*-line of sodium. The following mechanism is suggested: $Na + COCl_2 \rightarrow NaCl + COCl$; $Na + COCl \rightarrow NaCl^* + Na$; $NaCl^* + Na \rightarrow NaCl + Na + h\nu$.[158]

Molten sodium has been said to react with liquid carbon disulphide forming sodium sulphide[33] but another experiment indicates that no reaction occurs.[208]

Reactions of carbon disulphide with liquid ammonia solutions of sodium are described on page 520.

The action of sodium amalgam on carbon disulphide appears to be complicated.[208,209] In methylation experiments 1·5kg. of sodium amalgam was boiled with 450c.c. of carbon disulphide and, after removal of carbon disulphide, 2·5 l. of 90% alcohol was added to give a dark red solution through which was passed 80 l. of methyl chloride. The mixture was heated for 12hr. on a water bath, filtered hot to remove sodium chloride and evaporated to half its volume. The products were: dimethyldithiondithioloxalate or perthio-oxalate $(CS_2Me)_2$, and the compounds $CH_3OCS_2CH_3$ and $(CH_3)_2CS_3$, with some tetrakis(methylmercapto)ethylene. The formation of the compound $CH_3OCS_2CH_3$ is considered to be due to a side reaction.[208]

The diffusion flame technique has been used to study the reaction between sodium atoms and carbon disulphide vapour. At 270°C., with a partial pressure of sodium of 3×10^{-3}mm.Hg and a pressure of 1 to 10mm. for the inert carrier gas, the reaction velocity constant is about 0·0306c.c.mole^{-1}sec.$^{-1}$ $\times 10^{-11}$ and the collision number 200 to 500. The reaction is thus very slow. The product, CS_2Na, is probably formed by a third body collision mechanism. No chemiluminescence is observed.[158]

When ethylene is passed through a tube containing liquid sodium at 150°C. the ethylene is polymerized to a colourless liquid and sodium converted to a white brittle mass of sodium ethylene carbide. The accumulation of the sodium reaction product, which is inert towards ethylene, prevents further reaction. At higher temperatures the polymerization is accompanied by some decomposition of ethylene to acetylene and hydrogen, which react with sodium to form sodium acetylide, hydride and carbide. Free carbon and hydrogen are produced by the decomposition of acetylene; hydrogenation of ethylene and of the $:CH_2$ and $\vdots CH$ groups, formed by the splitting of ethylene or acetylene between the carbon atoms, accounts for the presence of small amounts of ethane and methane respectively in the exit gases.

The vapour pressure of sodium at 400°C. is sufficiently high for it to distil over and condense on the walls of the tube beyond the heating unit. The above reactions are thus summarized: $xC_2H_4 \rightarrow (C_2H_4)_x$, (150°C.); $C_2H_4 \rightarrow C_2H_2 + H_2$ (200°C.); $2Na + H_2 \rightarrow 2NaH$ (200°C.); $Na + C_2H_2 \rightarrow C_2HNa + 0{\cdot}5H_2$ (200°C.); $2C_2HNa \rightarrow Na_2C_2 + C_2H_2$ (210°C.); $C_2H_2 \rightarrow 2C + H_2$ (>200°C.). The results of experiments carried out in the temperature range 150° to 550° in the presence of sodium are given in Table XIII.

The low yield of acetylene at 550° C. is due to the reaction of sodium with acetylene to form acetylides and to the decomposition of acetylene to carbon and hydrogen.[210]

The effect of ethylene on the quenching of sodium resonance radiation, the rate of polymerization of ethylene in the presence and absence of such radiation and the effect of sodium surfaces or sodium vapour on the thermal

TABLE XIII. - REACTIONS OF ETHYLENE IN THE PRESENCE OF SODIUM

Temperature of tube, °C.	150	165	100-240	400	450	500	550
Duration of run, min.	37	50	-	53	45	35	33
Gas passed, c.c.	575	1066	-	660	525	620	420
Gas evolved, c.c.	580	1050	-	720	580	760	635
%C_2H_4 before expt.	98·4	98·0	98·0	98·0	98·0	98·0	98·0
%C_2H_4 after expt.	99·2	98·5	91·8	82·0	82·0	48·8	34·6
%Decomposition	0	0	6·3	16·4	16·4	50·5	64·7
Analysis of exit gas by volume							
%C_2H_4	99·2	98·5	91·8	82·0	82·0	48·8	34·6
%C_2H_2	-	-	6·2	2·5	1·7	0	5·4
%H_2	-	-	1·3	13·1	12·0	43·4	46·1
%CH_4	-	-	-	1·1	2·0	3·8	3·0
%C_2H_6	-	-	-	trace	trace	3·1	3·0
Total	99·2	98·5	99·3	98·7	97·7	99·1	99·1

polymerization of ethylene over a somewhat higher temperature range, have been investigated. Sodium metal is distilled into a cylindrical tube, previously evacuated at high temperatures, and is deposited on the walls as a bright metallic mirror. The tube is heated to the reaction temperature and illuminated with a Zeiss sodium lamp. The admission of ethylene at a pressure as low as 5mm. suffices to extinguish the visible fluorescence *i.e.* the energy of the excited sodium atoms is transferred to ethylene by collision. The results of tests carried out between 132° and 255°C. are shown in Table XIV.[213]

TABLE XIV. - PHOTOSENSITIZED POLYMERIZATION OF ETHYLENE BY SODIUM RESONANCE RADIATION

Temp. °C.	Pressure mm./25°C.	Time of illumination, h.	ΔP mm.
132	3·3	1·66	<0·1
184	4·8	10·0	<0·1
218	5·2	5·5	<0·1
255	5·25	5·0	<0·05
255	133·0	20·0	~1·0

At least 48kg.-cal. per mole are transferred to the ethylene molecules by collision with excited sodium atoms and although this is a larger amount of energy than that required as activation energy in the thermal polymerization process, 35 to 42kg.-cal. at 350° to 400°C.,[211,212] no observable polymerization occurs at 132° to 255°C. by sodium radiation.

The results of experiments carried out on the thermal polymerization of ethylene with and without sodium are shown in Table XV.[213]

TABLE XV. - THERMAL POLYMERIZATION OF ETHYLENE IN PYREX VESSELS WITH AND WITHOUT A COATING OF SODIUM

No. of expt.	Temp. °C.	Pressure mm.	ΔP mm.	Δt h	$\Delta P/\Delta t$	Remarks
1	302	182	20·6	44	0·46	Sodium present
2	302	154·8	26·4	63	0·42	Sodium present
3	302	167	2·4	38	0·06	Sodium absent
4	354	166	1·0	23	0·04	Sodium absent
5	354	180	22·0	17	1·3	Sodium present
6	354	183	26·5	22	1·2	Sodium present
7	302	184	23·8	70	0·34	Sodium present
8	354	182	30·3	21	1·4	Sodium present
9	255	181	23·0	232	0·1	Sodium present

The presence of sodium obviously catalyzes the polymerization; illumination with sodium resonance radiation in the above temperature range again produces no noticeable acceleration. The activation energy deduced from experiments 6, 7 and 8 is $E = 20$ kg.-cal., and from experiments 7 and 9 $E = 17$ kg.-cal. These values are lower than those of Pease[211] and Storch.[212]

The efficiency of resonance radiation with mercury at room temperature and cadmium at 200°C. in the acceleration of the polymerization of ethylene is associated with their ability to form free radicals which are efficient agents in the initiation of a polymerization chain. The mechanism of the thermal polymerization process is still obscure.[213]

Sodium reacts with acetylene to form acetylides and hydrogen: $2Na + C_2H_2 \rightarrow Na_2C_2 + H_2$; $\Delta H^\circ_{298} = -8{\cdot}396$ kg.-cal./mole.[33,214,215]

The dissociation pressures of sodium acetylide have been measured between 100° and 183°C., the following equation expresses the experimental results: $\log_{10}P(\text{mm.}) = 8{\cdot}538 - 2749/T$. The heat of dissociation deduced from this equation is +12·6 kg.-cal., which is higher than that obtained from the standard heats of formation of the reactants and products at 18°C.:

$2NaC_2H \rightleftharpoons Na_2C_2 + C_2H_2$; $\Delta H^\circ_{291} = 8{\cdot}2$ kg.-cal.[216]
2(25·1) (4·1) (54·3)

Sodium reacts with acetylene in liquid ammonia solution to form sodium acetylide: $C_2H_2 + Na \rightarrow CHCNa + 0{\cdot}5H_2$ (see page 522).

Atomic reactions of sodium with cyanogen and with cyanogen chloride and bromide have been investigated by the diffusion flame method. Although the reaction with cyanogen is exothermic, the collision yield is only 1 in 15,000 at 300°C. and 500°C.[38,97] Cyanogen chloride and bromide react to give sodium halide rather than the cyanide. Curry and Polanyi have shown that the primary reactions are: $Na + CNCl(Br) \begin{array}{l} \rightarrow NaCl(Br) + CN \\ \rightarrow NaCN + Cl(Br) \end{array}$ and that the ratio of NaCN: NaCl is not greater than 1:50 at a reaction temperature of 270° to 400°C. The secondary reaction, $Cl + Na_2 \rightarrow NaCl^* + Na$, produces sodium chloride molecules which carry most of the energy of the reaction and on collision with other sodium atoms excite them to emission of the D-line.[217]

Anhydrous hydrogen cyanide reacts with sodium amalgam in the presence of a solvent or suspension medium to form sodium cyanide. Alternatively the amalgam can be converted to alkoxide which is then used to react with hydrogen cyanide.[219]

The velocity constants for the reactions of sodium vapour with cyanogen fluoride, chloride and bromide as measured by the diffusion flame method of Hartel and Polanyi are in the ratio of 1:1·7:120.[218]

Fatty esters treated with sodium in the presence of a reducing alcohol such as *iso*butyl alcohol are converted into alkoxides which react with urea on refluxing at a temperature below 200°C. to yield a precipitate of sodium cyanate: $RONa + NH_2CONH_2 \rightarrow ROH + NaOCN + NH_3$.[220]

The oxide of cobalt is reduced by sodium to metallic cobalt, 97% of which remains in the alpha form at room temperature.[221]

The reduction of the dioxides of thorium, zirconium and titanium by sodium or calcium or a mixture of the two has been described by Ruff and Brintzinger.[222] The reaction is carried out in a wrought iron bomb and the results obtained for the reduction of thorium dioxide are given in Table XVI; the percentage of thorium in the product is obtained by measuring the volume of hydrogen evolved on treatment with hydrochloric acid: $Th + 4HCl \rightarrow ThCl_4 + 2H_2$. No reaction occurs below the boiling point of sodium in the absence of calcium, *i.e.* with 100% sodium. Optimum results are obtained by using 30% of sodium and 70% of calcium as reducing agent. A 90% yield of thorium of 96% purity has thus been obtained.

TABLE XVI. - REDUCTION OF THORIUM DIOXIDE WITH SODIUM AND CALCIUM

Wt. of ThO_2 g.	Wt. of reducing metals		% of Na in reducing metals	Temp. °C.	Time min.	Product	
	Na g.	Ca g.				Yield %	% Metallic thorium
5·288	0	2·3	0	900	20	89	61·8
5·288	0	3·5	0	950	20	99·6	60·1
5·288	0·5	3·0	12·5	900	15	94·7	69·09
5·288	0·5	3·0	12·5	950	20	95·4	74·59
5·288	0·9	2·6	23·0	950	20	91·0	82·30
5·288	1·2	2·5	29·4	950	20	92·7	84·12
5·288	1·2	2·5	29·4	950	60	92·7	84·38
5·288	2·0	1·8	49·1	900	20	91·4	74·32
5·288	3·5	0·5	85·8	870	10	85·8	42·94
5·288	3·5	0·5	85·8	900	20	82·7	44·21
5·288	4·0	0	100·0	875	10	–	–

The reduction of zirconium dioxide has been brought about in a similar way. Zirconium in the product is determined by measuring the hydrogen evolved on treatment with hydrogen fluoride: $Zr + 4HF \rightarrow ZrF_4 + 2H_2$.

The results of three experiments are given in Table XVII.

TABLE XVII. - REDUCTION OF ZIRCONIUM DIOXIDE WITH SODIUM AND CALCIUM

Wt. of ZrO_2 g.	Wt. of reducing metals		% Na in reducing metals	Temp. °C.	Time min.	Product	
	Ca g.	Na g.				Yield %	Zr %
2·452	3·5	0	0	950	20	99·99	85·5
2·452	2·5	1·2	29·4	950	20	99·99	97·25
2·452	0	4·0	100·0	950	20	91·15	25·68

A mixture of sodium and calcium containing about 30% of sodium is a more efficient reducing agent than either calcium or sodium alone.

Titanium dioxide has been reduced to the metal under similar conditions, as detailed in Table XVIII. No reduction is observed with sodium alone nor is the efficiency of the calcium reduction appreciably increased by the addition of sodium. The percentage of titanium in the product has been determined by measuring the volume of hydrogen evolved on treatment with hydrochloric acid: $2Ti + 6HCl \rightarrow 2TiCl_3 + 3H_2$.

TABLE XVIII. - REDUCTION OF TITANIUM DIOXIDE WITH SODIUM AND CALCIUM

Wt. of TiO_2 g.	Wt. of reducing metals		% Na in reducing metals	Temp. °C.	Time min.	Product	
	Ca g.	Na g.				Yield %	Ti %
1·60	3·5	0	0	950	20	95·8	82·5
1·60	2·5	1·2	29·4	950	20	97·0	83·05
1·60	0	4·0	100	900	20	–	–

Zirconium and similar refractory metals are obtained by heating together the oxide, ZrO_2, an alkali metal such as sodium and an alkali metal halide the base of which is different from the alkali metal used. Oxygen and nitrogen must be absent.[223]

Titanium and zirconium oxides are also reduced to the metals by heating with one or more alkali metals and calcium chloride.[224]

The reduction of chromium trioxide by sodium vapour is brought about by smelting a mixture of chromium trioxide and an oxygen compound of sodium, such as sodium carbonate, with carbon to liberate and volatilize sodium which reduces the oxide to chromium.[225]

The reduction of metallic oxides by sodium vapour is achieved by allowing sodium vapour to react with the oxide in the presence of coke and nitrogen or a carbonaceous and nitrogenous material, when the heat generated by the formation of sodium cyanide is used to bring about the reduction.[226]

Sodium reduces iron oxide below 1200°C. at atmospheric pressure; iron reduces sodium oxide at 550°C.[227]

High-surface sodium, deposited on a carrier, reduces metallic oxides to the metals. Dry zinc oxide is placed in a flask, the air of which is displaced with dry nitrogen, and sodium is added with stirring at 130°C. As soon as the sodium is dispersed over the surface of the oxide, the temperature is raised and although reduction begins at 130°C. to 150°C. it is necessary to heat at 230°C. to 300°C. to complete the reaction. The product is a mixture of colloidal zinc, sodium monoxide and unchanged zinc oxide. The finely divided zinc is isolated by washing with water. Metals prepared in this way are of colloidal dimensions and very reactive; when exposed to air they are pyrophoric and should therefore be used as formed in a continuous or semi-continuous process. Experimental data for iron, zinc and nickel oxides are given in Table XIX.[64]

TABLE XIX. - REDUCTION OF IRON, ZINC AND NICKEL OXIDES BY HIGH-SURFACE SODIUM

Compound	Sodium carrier	Reduction temp. °C.	Yield of metal %
Fe_2O_3	NaCl	100-200	>90
ZnO	ZnO	230-300	80-95
NiO	NaCl	300	-

Halla and Tompa have studied the system sodium/sodium hydroxide by means of thermal analysis, *X*-ray examination and chemical analysis.

Caustic soda is melted in a nickel crucible in an atmosphere of dry nitrogen freed from carbon dioxide, and the temperature of the melt kept at 450°C. for 3-4hr. to remove moisture. Small cubes of freshly cut sodium are thrown into the melt and the crucible quickly closed. Thorough mixing of the components is achieved by rotating the crucible about a horizontal axis for 24hr. at 400°C.; the crucible is then placed in a vertical position and thermal data collected during the cooling stage. When completely cold, the crucible is opened, and a drilling of the solidified melt quickly removed for chemical analysis. The melt, which is dark green, yields on solidification a homogeneous yellowish white crystalline aggregate which is sensitive to daylight, on exposure to which it becomes a green to greyish blue colour. Pure sodium hydride behaves in a similar way on exposure to daylight. *X*-Ray examination of the solidified melt shows the presence of sodium monoxide, sodium hydride and sodium hydroxide.

The reaction which occurs when sodium is added to sodium hydroxide under the above conditions is given by the equation: $2Na + NaOH \rightarrow Na_2O + NaH$.

In the course of this work the m.p. of pure sodium hydroxide has been shown to be 327·6 ± 0·9°C. and the effect of water and sodium carbonate on the melting point determined; $t = 327{\cdot}6 - 0{\cdot}196p - 0{\cdot}0011p^2 - 0{\cdot}30w$, where p is the sodium carbonate content expressed as g. per 1000g. of melt, and w is the water content.

The composition of the melt has been determined as follows: a known weight is dissolved in water and a portion of the standard solution titrated with 0·1N. hydrochloric acid in the presence of methyl-orange. Another portion is treated with barium chloride and titrated with 0·1N. oxalic acid with phenolphthalein as indicator. The difference between the two titrations is used to calculate the sodium carbonate content. A portion of the solidified melt is treated with water and the volume of hydrogen evolved is measured to determine the sodium hydride content. If 1g. of melt contains xg. of sodium carbonate and yg. of sodium hydride and produces zg. of sodium hydroxide in solution in water, then the weight of sodium monoxide $= \frac{62}{18}[z - (1 - x) - \frac{2}{3}y]$.

In Table XX the solidification temperatures in column 6 have been corrected for sodium carbonate content.

TABLE XX. - ARREST POINTS IN THE SYSTEM SODIUM-SODIUM HYDROXIDE

No. of expt.	Na added	1000g. Solid melt contains			Arrest points °C.		
		NaH g.	Na_2O g.	Na_2CO_3 g.	Solidification point corrected	Transition point	Eutectic point NaOH
6	Slight	0	?	15	317·7	293·7	-
7	Slight	0	?	13	319·6	293·0	-
9	Large	20?	59	32	321·1	280·5	271·7
11	Large	19·5	-	25·4	319·2	282·4	273·4
14	Large	10·2	56	41	324·4	292·8	277·8
27	Large	12·2	-	10·2	318·7	289·2	273·4
35	Large	33	60	2·8	319·9	281·4	275·7
37	Large	29	-	5	327·0	282·3	-
28	Na_2O	-	41·3	4·8	301·4	293·5	-

Since the molecular ratio of sodium hydride to sodium monoxide in the melt should be 1·0, it is apparent from the figures given in Table XX that the apparatus was not completely gas-tight (test 9, 0·88, test 14, 0·65) and that in some cases (tests 11, 27, 35, 37) there was an error in the estimation of hydride and oxide content.[228]

The action of sodium on sodium hydroxide has been investigated more recently by Williams[70] by heating the mixture in stainless steel vessels up to 600°C. or in nickel vessels up to 700°C.

If the components are heated in an evacuated system at temperatures up to 385°C., hydrogen is evolved according to the dissociation pressure of sodium hydride until all the sodium hydroxide has been converted into sodium monoxide.

When the components are heated in a closed system above 385°C., an equilibrium is established which does not correspond to the dissociation pressure diagram for sodium hydride, and this new equilibrium appears to be related to the solubility of the reaction products in sodium and sodium hydroxide. The system appears to be influenced by a number of simultaneous reactions: $2Na + NaOH \rightleftharpoons Na_2O + NaH$; $NaH \rightleftharpoons Na + 0{\cdot}5H_2$; $H_2 + Na_2O \rightleftharpoons NaOH + NaH$.

Fig. 5 shows a typical sodium-sodium hydroxide reaction curve obtained by plotting the pressure of hydrogen evolved against the reaction temperature. The dome shaped plateau and the reabsorption dip occur at the same pressures and temperatures even when the ratio of sodium to sodium hydroxide is varied from 1:4 to 8:1. When the system at about 550°C. is cooled, the cooling curve as shown in Fig. 6 returns linearly until a temperature of about 385°C. is reached; it then proceeds along the heating curve. The hump of the heating curve is therefore a quasi-equilibrium region where two or more competing reactions are taking place.

The rise in pressure beyond 600°C. shown in Fig. 5 is due to attack on the

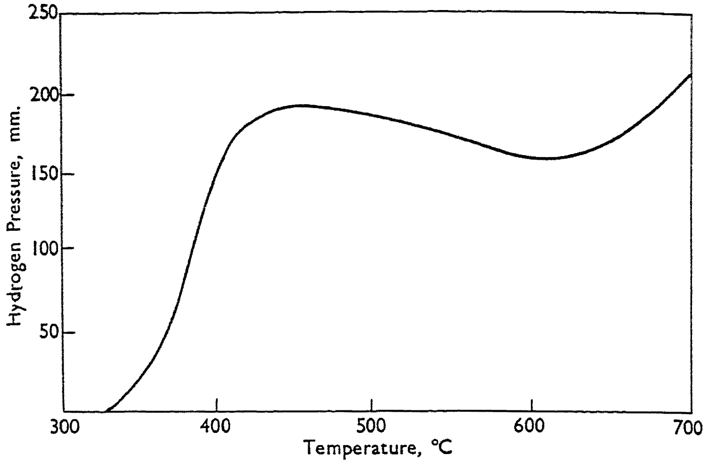

FIG. 5. TYPICAL SODIUM-SODIUM HYDROXIDE REACTION CURVE

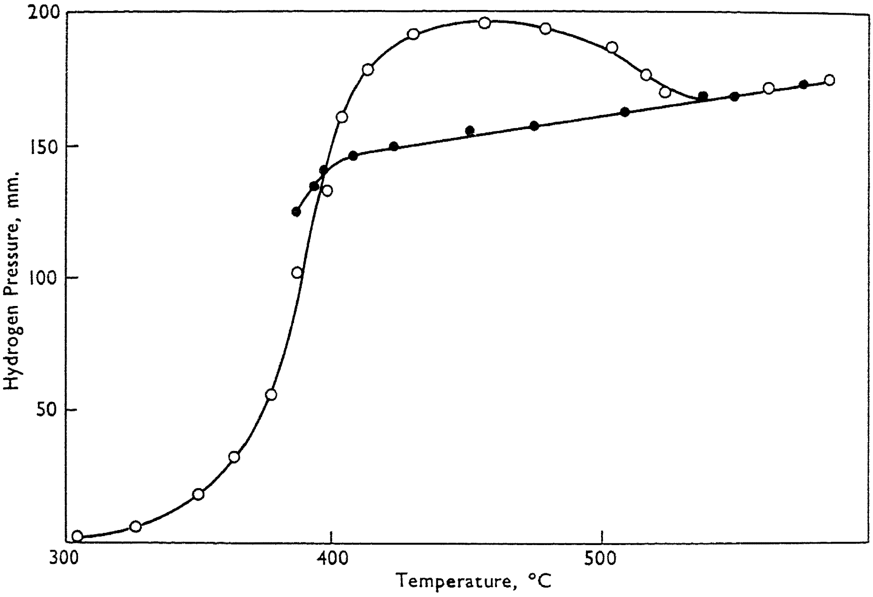

FIG. 6. QUASI-EQUILIBRIUM IN SODIUM-SODIUM HYDROXIDE REACTION
⊙ Heating curve; ● Cooling curve.

stainless steel pot and to a further direct release of hydrogen from sodium hydride.

The presence of an inert gas depresses the dissociation of sodium hydride in the sodium–sodium hydroxide reaction as may be seen from Fig. 7.

The system sodium–hydrogen–sodium hydroxide–sodium monoxide has also been studied by Klemenc and Svetlik. The reduction of sodium monoxide with hydrogen begins at 110°. A method is also given for the determination of sodium hydride formed in the system.[229]

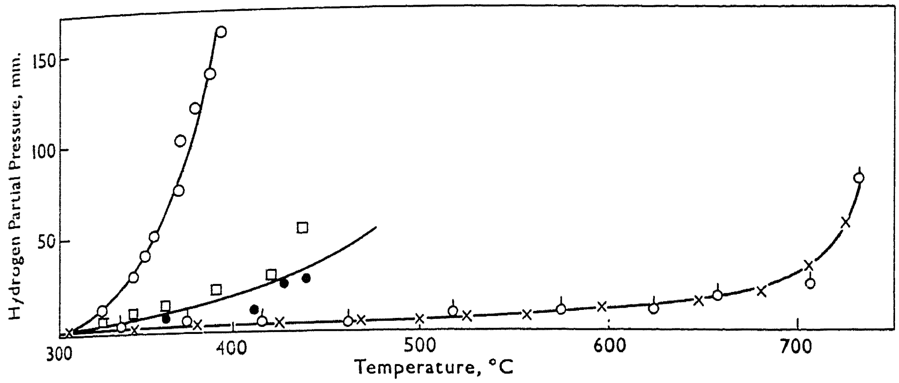

FIG. 7. EFFECT OF INERT GAS PRESSURE ON THE SODIUM-SODIUM HYDROXIDE REACTION AND THE DISSOCIATION OF SODIUM HYDRIDE
○ NaH + vacuum; □ NaH + 760mm. nitrogen; ● NaH + 760mm. argon;
X Na + NaOH + 760mm. nitrogen; ♁ Na + NaOH + 380mm. nitrogen.

Sodium hydroxide, sodium oxide, sodium, sodium hydride and hydrogen are obtained as an equilibrium mixture when sodium hydride is dissolved in molten sodium hydroxide. Where there is a gaseous phase, hydrogen, and only one condensed phase, the system is defined by the temperature, pressure and one composition variable. The equilibrium hydrogen pressure has been determined as a function of the composition of the condensed phase or phases for equilibrium mixtures with original compositions of 2·5–97·5, 5·0–95·0, 10·0–90·0 and 20–80mole-% of sodium hydride in sodium hydroxide at 600°, 700° and 800°C. The equilibrium hydrogen pressure–composition isothermals obtained by removing measured increments of hydrogen have been reproduced by allowing hydrogen to be reabsorbed; results for the 5·0mole-% sodium hydride mixture have been duplicated by starting with an equivalent quantity of sodium in sodium hydroxide and allowing the mixture to react with measured increments of hydrogen.[230]

The estimation of hydrogen in sodium hydroxide by reduction with sodium at 700°C. has been described by Pepkowitz and Proud[231] to demonstrate a micromethod for the determination of hydrogen in its compounds. Typical results are given in Table XXI.

TABLE XXI. - HYDROGEN RECOVERIES FROM SODIUM HYDROXIDE
$2Na + 2NaOH = 2Na_2O + H_2$

Wt. of sample mg.	Hydrogen present mg.	Hydrogen released mg.	ΔH_2 mg.
2·9	0·070	0·074	Average ΔH = ±0·008
3·0	0·075	0·069	
3·4	0·085	0·094	
3·6	0·090	0·086	
8·2	0·205	0·210	
8·2	0·205	0·184	
9·3	0·230	0·222	
20·4	0·510	0·519	

Sodium vapour passed in counter-current through molten potassium hydroxide under reduced pressure reduces the hydroxide to potassium; the resultant metal vapours condense to form sodium-potassium alloys from which potassium may be isolated by fractionation.[232]

The system $Na + KOH \rightleftharpoons K + NaOH$ has been investigated by Rinck.[233] The materials employed are described as pure industrial products; the hydroxide was, however, subjected to a prolonged fusion in a silver capsule to remove moisture before use.

The required quantities were introduced into a well dried steel tube, which was sealed and placed in an already heated furnace. When a temperature of about 400° C. was attained, the mixture was energetically shaken for 20 to 30 min. in a horizontal position by a mechanical device and the tube then placed in a vertical position for the same length of time to facilitate separation of the two liquid phases, the light layer of sodium-potassium alloy and the heavier layer of the two hydroxides. The system was then rapidly chilled by submerging the tube in cold water. The stopper was sawn off and the liquid sodium-potassium alloy poured in small amounts at a time into absolute alcohol; when the reaction was complete, water was added and the solution analyzed for total alkalinity and for potassium by the perchlorate method while sodium was calculated by difference.

The mixed hydroxides were contaminated with the liquid phase but measurement of the hydrogen evolved on treatment with water gave the necessary data for calculation of the amount present. The solution was diluted and tested for total alkalinity and potassium, sodium being determined by difference.

TABLE XXII. - 400° ISOTHERM OF THE EQUILIBRIUM REACTION
$Na + KOH \rightleftharpoons K + NaOH$

Initial state mol. ratio KOH/Na	Final state metallic phase		Hydroxide phase		Equilibrium Constants	
	atom-%K	atom-%Na	mol.-%KOH	mol.-%NaOH	*C*	*K*
0·102	10·1	89·9	7·48	93·52	0·71	0·354
0·102	10·4	89·6	7·02	92·98	0·65	0·323
0·102	10·8	89·2	6·96	93·04	0·62	0·307
0·138	12·6	87·4	10·0	90·0	0·77	0·405
0·138	12·9	87·1	10·3	89·7	0·77	0·408
0·138	13·3	86·7	9·1	90·9	0·65	0·425
0·205	16·8	83·2	12·7	87·3	0·72	0·396
0·205	16·8	83·2	11·1	88·9	0·60	0·319
0·205	17·9	82·1	12·0	88·0	0·62	0·342
0·205	17·9	82·1	13·8	86·2	0·73	0·416
0·224	18·8	81·2	13·9	86·1	0·70	0·401
0·362	29·8	70·2	16·5	83·5	0·47	0·288
0·410	31·9	68·1	20·8	79·2	0·56	0·371
0·410	33·1	66·9	23·4	76·6	0·62	0·432
0·419	33·3	66·7	22·6	77·4	0·59	0·404
0·410	34·3	65·7	17·7	82·3	0·41	0·260
0·410	35·1	64·9	16·9	83·1	0·38	0·238
0·818	52·4	47·6	34·4	65·6	0·48	0·413
0·791	53·0	47·0	36·4	63·6	0·51	0·452
0·821	54·2	45·8	31·1	68·9	0·38	0·315
0·818	54·4	45·6	29·3	70·7	0·35	0·283
0·807	54·9	45·1	31·0	69·0	0·37	0·307
0·818	55·0	45·0	35·4	64·6	0·45	0·395
0·818	55·8	44·2	30·1	69·9	0·34	0·279
0·954	61·2	38·8	35·5	64·5	0·35	0·317
1·21	66·2	33·8	44·1	55·9	0·40	0·412

continued on the following page

TABLE XXII (continued)

Initial state mol. ratio KOH/Na	Final state metallic phase		Hydroxide phase		Equilibrium Constants	
	atom-%K	atom-%Na	mol.-%KOH	mol.-%NaOH	C	K
1·27	69·0	31·0	44·6	55·4	0·36	0·378
1·54	73·0	27·0	51·5	48·5	0·39	0·453
1·60	74·3	25·7	51·9	48·1	0·37	0·435
1·65	75·3	24·7	49·1	50·9	0·32	0·367
1·53	77·2	22·8	51·2	48·8	0·31	0·385
1·85	79·8	20·2	55·5	44·5	0·32	0·405
2·46	84·4	15·6	69·9	30·1	0·43	0·644
2·68	85·6	14·4	69·1	30·9	0·38	0·569
mol. ratio NaOH/K						
1·96	44·2	55·8	29·1	70·9	0·52	0·405
0·98	61·6	38·4	38·5	61·5	0·39	0·350
				Average	0·50	0·379

The results are given in Table XXII where the equilibrium constant C has been calculated on the assumption that the 'perfect' law of mass action holds. Lorentz's law of mass action, governing condensed systems and based on an equation of state analogous to that of van der Waals has been used to calculate the equilibrium constant, K. The constant C is found to vary from 0·77 to 0·31 but K also varies and in this case from 0·644 to 0·238.

Slight carbonation always occurs when the alkali hydroxides are manipulated in air, so that the results obtained by Rinck refer to the equilibrium between potassium, sodium and very dilute solutions of the metal carbonates in caustic alkalis. The concentration of the carbonates can vary from one experiment to another so that the equilibrium constant must also vary. The main reaction, $Na + KOH \rightleftharpoons NaOH + K$, is therefore accompanied by the secondary reaction, $2Na + K_2CO_3 \rightleftharpoons Na_2CO_3 + 2K$. Also, analysis of the hydroxide phase includes an appreciable error due to the conversion of some of the alkali metal to oxide, hydroxide and carbonate and to the solubility of the alkali metals in their compounds.

Rinck concludes that there is no reason to suppose that the above equilibrium does not obey the 'perfect' law of mass action and he gives a value of 0·50 for the equilibrium constant $C = [Na][KOH]/[K][NaOH]$ at 400° to 700°C. During this work the densities of sodium and potassium were found to be: $d_t = 0{\cdot}9385 - 0{\cdot}000260(t - 96{\cdot}5)$ for sodium and $d_t = 0{\cdot}826 - 0{\cdot}000222(t - 62{\cdot}5)$ for potassium.[233]

Halla and Tompa show that the upper limit for the equilibrium constant at 400°C. for the reaction: $K_2O + Na \rightleftharpoons Na_2O + K$ is 0·434.[234]

The reaction between fused sodium and potassium and their fluorides has been studied by Rinck at 1000° C. Preliminary experiments show that at this temperature steel is badly attacked but thick walled nickel tubes are satisfactory. The fluoride is dehydrated before use and although equilibrium at 1000° C. is reached in about 2-3min., shaking for 10 min. before the tube is placed in a vertical position allows the light metal phase and the heavier fluoride phase to separate. The system is then preserved by rapidly chilling and the metal and fluoride phases analyzed, the former by the method already described in the metal-hydroxide reaction above and the latter as follows. Since the fluoride phase always contains some of the alloy, the total alkalinity of its aqueous solution is determined and expressed as potassium fluoride; potassium is determined by the perchlorate method and expressed as potassium fluoride; total fluorine is estimated as calcium fluoride and from these determinations the amounts of sodium fluoride and potassium fluoride can be obtained. The experimental figures are very similar to those calculated from the composition of the starting materials and that of the metal phase, from which it is concluded that the metals dissolve in the mixed fluorides in the same ratio as they are alloyed in the metallic phase. The experimental results given in Table XXIII[233] include also those for four ternary mixtures, and the average value for the equilibrium constant $C = [\mathrm{Na}][\mathrm{KF}]/[\mathrm{K}][\mathrm{NaF}] = 0{\cdot}29$ at 1000° C.[233,235]

TABLE XXIII. - 1000° C. ISOTHERM OF THE EQUILIBRIUM REACTION $\mathrm{Na} + \mathrm{KF} \rightleftharpoons \mathrm{K} + \mathrm{NaF}$

Initial state mol. ratio KF/Na	Final state				Equilibrium constant C
	Metallic phase		Salt phase		
	atom-%K	atom-%Na	mol.-%KF	mol.-%NaF	
0·119	14·6	85·4	5·26	94·74	0·326
0·198	19·1	80·9	5·99	94·01	0·270
0·283	27·0	73·0	9·83	90·17	0·295
0·396	34·4	65·6	15·7	84·3	0·356
0·396	34·6	65·4	11·1	88·9	0·236
0·396	35·5	64·5	16·0	84·0	0·348
0·440	38·5	61·5	19·2	80·8	0·380
0·495	42·0	58·0	19·2	80·8	0·328
0·495	45·1	54·9	19·7	80·3	0·298
0·660	52·6	47·4	28·6	71·4	0·361
0·990	64·2	35·8	37·6	62·4	0·335
0·990	65·2	34·8	33·9	66·1	0·261
1·32	78·3	21·7	44·7	55·3	0·224
1·585	80·0	20·0	53·9	46·1	0·294
1·98	85·6	14·4	56·6	43·4	0·219
mol. ratio NaF/K					
1·86	52·0	48·0	26·5	73·5	0·333
0·931	66·5	33·5	37·8	62·2	0·306
0·466	77·3	22·7	45·5	54·5	0·246
Ternary mixtures					
Na KF NaF					
0·218 0·017 0·119	7·09	92·89	1·90	98·10	0·254
0·131 0·038 0·119	22·6	77·4	6·92	93·08	0·255
Na K KF					
0·044 0·026 0·121	91·31	8·69	69·0	31·0	0·212
0·044 0·026 0·172	94·87	5·13	82·5	17·5	0·255
					Average 0·29

Equilibria between sodium and potassium and their chlorides in the fused state have been studied by Jellinek and Tomoff.[236] The alkali metal is dissolved in molten lead and the sodium-lead alloys heated at 800° C. with potassium chloride in a refractory crucible. The proportions of the reactants are varied and the product is analyzed at intervals of 6min. For a given mixture the ratio of sodium to potassium in the solid phase is found to be constant. The reaction, $\mathrm{Na} + \mathrm{KCl} \rightleftharpoons \mathrm{K} + \mathrm{NaCl}$ is shown to be an equilibrium reaction governed by the law of mass action such that $\frac{[\mathrm{Na}]}{[\mathrm{K}]} \cdot \frac{[\mathrm{KCl}]}{[\mathrm{NaCl}]} = 12{\cdot}2$ (the average of 10·4, 11·4 and 14·8) at 800° C. The concentrations of the alkali metals,

[Na], [K] are expressed as the number of atoms per 100 atoms of alkali metal dissolved in the lead, and [NaCl], [KCl], as the number of molecules of each chloride per 100 molecules of total chloride in the salt phase. By carrying out the reaction in this manner, the alkali metal-lead alloy, which is very heavy, settles to the bottom leaving the mixture of fused chlorides at the top of the crucible.

Jellinek and Czerwinski[237] have also studied the above reaction. Salt mixtures of definite composition are fused above molten lead (which serves as a cathode) in such amounts that on electrolysis, using a carbon rod as anode, no appreciable change takes place in the salt mixture owing to the deposition of metal. The lead-sodium alloy and potassium chloride are then allowed to react at 1000°C. The equilibrium is shown to conform to the law of mass action and $\frac{[Na][KCl]}{[K][NaCl]}$ is 11·1 at 1000°C. (average of 13·0, 11·2 and 9·0) (see also Fig. 8 page 486). Hackspill and Rinck[233,238] in their work on the equilibrium reaction: $Na + KCl \rightleftharpoons K + NaCl$, have dispensed with the solvent, molten lead, and heated the components at 900°C. in a sealed iron tube which is shaken vigorously in a horizontal position by a mechanical device. Although equilibrium is attained in a short time, the mixture is heated and shaken for 30min. after which it is placed vertically for another 30min. to facilitate the separation of the liquid phases. The system is rapidly chilled and on opening the tube the liquid metal alloy phase is found on the top and the halide phase at the bottom. The alloy phase is analyzed for total alkalinity and for potassium.

Although the separation of the two phases is generally satisfactory, the halide ingot still contains a certain amount of the alkali metals in the form of droplets of alloy in the crevices of the salt; this alloy has the composition of the metallic phase. A metallic mist is also uniformly distributed throughout the mass. Fused alkali chlorides dissolve appreciable quantities of potassium and sodium and on solidification the metals separate out and remain dispersed.

About 1g. of the salt is powdered and treated with absolute alcohol to dissolve out the metals, and when the hydrogen evolution has ceased, the mass is washed with alcohol and dissolved in water. The total alkalinity is determined, and assuming that the alkalinity is due to the presence of a mixture of sodium and potassium of the same composition as the metallic phase, the amount of potassium to which the hydroxide is equivalent can be calculated. The total potassium is determined by the perchlorate method and the result calculated as potassium chloride from which the amount corresponding to the metallic potassium dissolved is deducted. The total chloride is found and also the sodium by the uranyl acetate method.

The experimental results are given in Table XXIV.

The equilibrium constant C is calculated from the 'perfect' law of mass action, K from Lorentz's law of mass action governing condensed systems and based on an equation of state analogous to that of van der Waals.

The reaction $Na + KCl \rightleftharpoons K + NaCl - 6{\cdot}7$ kg.-cal. is endothermic at ordinary temperatures; the calculated value at 900°C. is -8 kg.-cal. Reduction in temperature should therefore favour the formation of sodium and potassium chloride with the disappearance of potassium and sodium chloride and this is confirmed by the finding that the equilibrium constant C at 800°C. is 14 whereas at 900°C. it is 11·5. Since the equilibrium constant K varies more than the constant C it is considered that within experimental error the equilibrium $Na + KCl \rightleftharpoons K + NaCl$ is governed by the 'perfect' law of mass action.

Potassium or potassium-sodium alloys are formed by continuously passing

TABLE XXIV. - 900°C. ISOTHERM FOR THE EQUILIBRIUM REACTION

$Na + KCl \rightleftharpoons K + NaCl$

Initial state mol. ratio KCl/Na	Final state				Equilibrium constants	
	Metallic phase		Salt phase			
	atom-%K	atom-%Na	mol.-%KCl	mol.-%NaCl	*C*	*K*
0·074	6·45	93·55	45·7	54·3	12·2	16·1
0·103	8·54	91·46	52·9	47·1	12·0	17·7
0·123	9·20	90·80	51·1	48·9	10·3	14·3
0·154	9·74	90·26	55·3	44·7	11·5	16·9
0·185	10·9	89·1	59·3	40·7	11·9	18·2
0·231	11·8	88·2	62·5	37·5	12·5	19·7
0·207	12·0	88·0	62·6	37·4	12·3	19·4
0·308	12·9	87·1	63·7	36·3	11·9	18·9
0·463	14·1	85·9	68·5	31·5	13·7	22·0
0·463	15·4	84·6	69·7	30·3	12·6	21·0
0·617	17·9	82·1	71·2	28·8	11·3	19·0
0·463	18·2	81·8	67·7	32·3	9·4	15·1
0·925	25·2	74·8	77·2	22·8	10·1	17·4
1·234	27·8	72·2	79·9	20·1	10·3	18·0
1·542	29·9	70·1	82·6	17·4	11·1	19·6
1·850	33·0	67·0	82·1	17·9	9·3	16·1
3·084	38·9	61·1	88·9	11·1	12·6	23·0
mol. ratio NaCl/K						
0·736	38·6	61·4	88·6	11·4	12·4	22·1
0·448	60·0	40·0	94·3	5·70	11·0	17·3
0·321	76·6	23·4	97·47	2·53	11·8	16·1
0·221	91·0	9·0	99·12	0·88	11·1	12·4
				Average	11·5	18·1

molten potassium chloride into a reaction column at atmospheric pressure along with sodium vapour. The potassium vapour or potassium–sodium vapour rises and passes into a condensation chamber from which the metal or alloy is removed in the solid state. The sodium-rich slag is removed from the bottom of the reaction chamber and recycled to the sodium vaporizer.[239]

The equilibrium in the fused state between sodium, potassium and their bromides has been investigated by Rinck[233,240] at 800°C. The bromides are first dehydrated by fusion in a platinum crucible and the procedure is then similar to that employed for sodium, potassium and their hydroxides (see page 478). As may be seen from Table XXV, the equilibrium constant *C*, calculated from the simple law of mass action, fluctuates irregularly about an average value of 28·9, the deviation being less than 20%, whereas the equilibrium constant *K*, calculated from Lorentz's law governing condensed systems, varies about an average value of 13·1 with a deviation exceeding 25%. Rinck considers that the system is best represented by the simple mass action law and that the equilibrium constant at 800°C. = $[Na][KBr]/[K][NaBr] = 28{\cdot}9$.

Equimolecular amounts of sodium and potassium iodide have been heated together at 725°C. in a sealed tube in a rotary furnace and the reaction products rapidly chilled and analyzed. The ratio of sodium to potassium in the metallic phase is 10:1.[241]

In the fused state potassium iodide and sodium iodide are miscible in all proportions and all mixtures are liquid at temperatures above 682°C. Rinck[233] has studied the reaction: $Na + KI \rightleftharpoons NaI + K$ at 800°C., making use of the

TABLE XXV. - 800°C. ISOTHERM OF THE EQUILIBRIUM REACTION
$Na + KBr \rightleftharpoons K + NaBr$

Initial state mol. ratio KBr/Na	Final state				Equilibrium constants	
	Metallic phase		Salt phase			
	atom-%K	atom-%Na	mol.-%KBr	mol.-%NaBr	*C*	*K*
0·065	4·36	95·64	54·4	45·6	26·2	15·8
0·135	6·26	93·74	66·6	33·4	29·9	14·7
0·193	6·91	93·09	65·8	34·2	25·9	13·2
0·250	7·82	92·18	70·8	29·2	28·6	13·6
0·274	8·07	91·93	72·9	27·1	30·6	14·1
0·386	8·87	91·13	73·4	26·6	28·4	13·4
0·386	9·18	90·82	77·5	22·5	34·1	14·8
0·405	9·54	90·46	77·2	22·8	32·1	14·2
0·553	10·1	89·9	75·8	24·2	27·9	12·6
0·553	11·0	89·0	77·8	22·2	28·4	12·4
0·773	12·1	87·9	80·6	19·4	30·2	12·8
0·773	12·7	87·3	81·4	18·6	30·1	12·7
0·720	13·0	87·0	80·1	19·9	26·8	11·5
0·773	13·4	86·6	80·9	19·1	27·4	11·6
1·02	15·8	84·2	83·7	16·3	27·4	11·3
1·29	20·3	79·7	85·6	14·4	23·4	9·7
mol. ratio NaBr/K						
1·14	8·71	91·29	76·0	24·0	33·0	15·9
0·76	24·9	75·1	91·8	8·2	33·8	13·2
0·58	35·6	64·4	94·23	5·77	29·6	12·1
0·355	65·9	34·1	97·97	2·03	25·0	13·2
0·127	83·1	16·9	99·7	0·3	–	–
				Average	28·9	13·1

technique already described for the sodium–sodium hydroxide reaction (see page 478). Two phases separate, the top layer being an alloy of sodium and potassium, the bottom layer a mixture of sodium and potassium iodides.

Analysis of the metal phase is carried out by determining the total alkalinity, potassium as perchlorate and sodium by difference.

The salt phase is contaminated with the alkali metals dispersed throughout the mass, and a small quantity of the salts is dissolved in water and the solution tested in the following manner: the total alkalinity is determined and on the assumption that the sodium and potassium present are in the same ratio as in the metallic phase, the weight of potassium dissolved in the salts can be calculated. Potassium, determined as perchlorate, is calculated as potassium iodide; the quantity of potassium iodide equivalent to the dissolved metal is subtracted; total iodine is estimated and sodium iodide calculated. The results are given in Table XXVI.

The sodium–sodium halide systems have been studied by Bredig, Johnson and Smith[242] who state that no solid halides such as Na_2X have been found to exist.

The equilibrium between sodium, calcium and their chlorides in the fused state has been studied by Lorentz and Winzer.

Pure sodium and anhydrous calcium chloride ($CaCl_2$, 99·30%; CaO, 0·05%; SiO_2, 0·12% with a trace of aluminium) were heated with sodium chloride in a sealed tube and the equilibrium state was fixed by chilling the melt and breaking the tube under ether. The metal, which readily separates from the

TABLE XXVI. - 800°C. ISOTHERM OF THE EQUILIBRIUM REACTION
$Na + KI \rightleftharpoons K + NaI$

Initial state mol. ratio KI/Na	Final state				Equilibrium constant *C*
	Metallic phase		Salt phase		
	atom-%K	atom-%Na	mol.-%KI	mol.-%NaI	
0·069	3·18	96·82	65·9	34·1	58·7
0·139	4·03	95·97	71·1	28·9	58·5
0·277	5·66	94·34	79·5	20·5	64·6
0·462	6·49	93·51	83·8	16·2	74·3
0·924	11·4	88·6	86·7	13·3	50·6
1·848	15·3	84·7	92·31	7·69	66·5
mol. ratio NaI/K					
1·740	2·95	97·05	56·4	43·6	42·6
1·305	4·02	95·98	69·1	30·9	53·4
1·305	5·37	94·63	72·1	27·9	45·6
0·870	16·6	83·4	92·11	7·89	58·9
0·870	16·8	83·2	93·34	6·66	69·6
0·745	28·8	71·2	95·83	4·17	56·8
0·745	29·0	71·0	94·55	5·45	42·5
0·653	33·4	66·6	96·43	3·57	53·9
0·653	34·2	65·8	96·03	3·97	46·6
0·522	48·0	52·0	98·16	1·84	57·8
0·435	58·1	41·9	98·64	1·36	52·3
0·261	80·1	19·9	99·61	0·39	63·8
0·174	86·6	13·4	99·77	0·23	67·4
0·131	88·6	11·4	99·69	0·31	41·5
				Average C	56·3

$[Na][KI]/[K][NaI] = 56$ at 800°C.

salt phase, was treated first with methanol to remove sodium and then with water, the calcium being finally precipitated as oxalate and weighed as calcium sulphate.

The results are given in Table XXVII which also includes the solubilities of the metals in the melts. The latter have been found by treating the salt phase with water and titrating the alkali formed with 0·1N-HCl using methyl orange as indicator. The solubilities of calcium plus sodium are expressed as g. of sodium per 100g. of melt. There is a miscibility gap in the curve, cf. Fig. 8, in the region 16–98·5% calcium chloride; no variations other than those due to analytical errors can be detected for a temperature interval of over 300°.[243,244]

The system has been examined in the presence of lead or antimony by the same authors.[245]

Very pure lead and bright metallic sodium are melted together in a stream of dry, oxygen-free nitrogen in graphite crucibles and the sodium–lead alloy cast in bars by pouring into 'Supremax' tubes heated at 500°C.

Calcium chloride and the alloy are heated together in glass tubes which are drawn to a capillary but are sealed only after heating to the required reaction temperature. After chilling to preserve the equilibrium state the salt and metal phases are analyzed.

In Table XXVIII, atom-%Na or Ca in columns 2 and 3 refers to the ratio Na/Na + Ca or Ca/Na + Ca, no regard being paid to the lead used as a diluent.

The equilibrium, $Ca + 2NaCl \rightleftharpoons CaCl_2 + 2Na$ is displaced to the right

TABLE XXVII. - EQUILIBRIUM Ca + 2NaCl $\rightleftharpoons$ $CaCl_2$ + 2Na

Temp. °C.	Salt phase		Metal phase		Solubility of Na + Ca expressed as wt.-% Na in the melt
	$CaCl_2$ mol.-%	NaCl mol.-%	Ca atom-%	Na atom-%	
800	0	100	0	100	3·4
	0	100	0	100	5·4
	0	100	0	100	3·2
	0	100	0	100	4·3
	0	100	0	100	4·8
	3·3	96·7	0·11	99·89	4·6
	6·9	93·1	0·31	99·69	4·8
	10·0	90·0	0·34	99·66	4·5
	13·0	87·0	0·50	99·50	5·0
	15·2	84·8	0·75	99·25	5·0
	18·5	81·5	0·75	99·25	4·9
	19·9	80·1	0·79	99·21	5·0
	29·9	70·1	0·87	99·13	5·2
	34·9	65·1	0·98	99·02	5·4
	32·0	68·0	0·29	99·71	6·0
	41·6	58·4	0·71	99·29	5·6
	55·8	44·2	0·94	99·06	5·9
	62·5	37·5	0·88	99·12	6·1
	65·1	34·9	1·70	98·30	6·4
	75·4	24·6	0·70	99·30	6·3
	86·5	13·5	0·93	99·07	6·9
	90·4	9·6	0·85	99·15	6·3
	90·9	9·1	0·59	99·41	7·0
	91·4	8·6	0·93	99·07	6·6
	95·5	4·5	0·99	99·01	7·0
	96·6	3·4	0·89	99·11	7·2
	51·7	48·3	0·96	99·04	6·0
	97·1	2·9	0·89	99·11	9·1
700	66·5	33·5	0·75	99·25	3·4
	66·4	33·6	0·69	99·31	4·7
	53·2	46·6	0·74	99·26	4·6
	42·8	57·2	0·56	99·44	4·5
	33·8	66·2	0·52	99·48	4·3
	34·2	65·8	0·44	99·56	4·2
600	52·7	47·3	1·20	98·80	3·3
	53·5	46·5	0·91	99·09	2·7
	44·2	55·8	0·49	99·51	2·7
500	51·9	48·1	0·51	99·49	0·4
	51·6	48·4	0·88	99·12	0·6
	50·6	49·4	0·94	99·06	1·2
	52·0	48·0	0·87	99·13	0·4

when lead is added to the metal phase and the displacement increases until the ratio Pb/(Na + Ca) is about 8; the addition of more lead produces no further change.

The results obtained by adding antimony to the metal phase are given in Table XXIX.

The equilibrium is displaced by the addition of antimony in the same way as with lead but the magnitude of the displacement is different.

Since sodium and calcium chloride are more readily attacked by air than are calcium and sodium chloride, Rinck,[233,246] in investigating the reaction

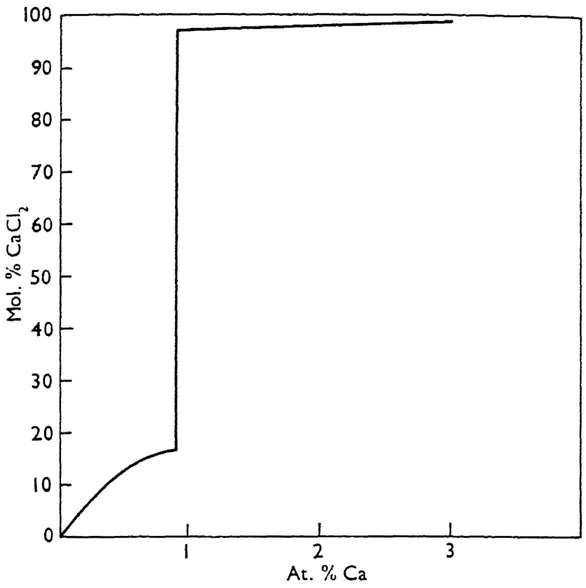

FIG. 8. 850° ISOTHERM: $2NaCl + Ca \rightleftharpoons CaCl_2 + 2Na$

TABLE XXVIII. - EQUILIBRIUM: $Ca + 2NaCl \rightleftharpoons CaCl_2 + 2Na$ (800°C.) WITH THE ADDITION OF LEAD TO THE METAL PHASE

Pb/(Na + Ca) in atoms	Ca at.-%	Na at.-%	CaCl$_2$ mol.-%	NaCl mol.-%
15·8	6·7	93·3	8·6	91·4
15·8	51·6	48·4	49·7	50·3
15·8	17·0	83·0	15·8	84·2
15·8	65·8	34·2	65·1	34·9
15·8	28·2	71·8	25·3	74·7
15·8	90·5	9·5	95·0	5·0
8·5	3·0	97·0	3·5	96·5
8·5	8·8	91·2	15·8	84·2
8·5	32·3	67·7	33·0	67·0
8·5	46·4	53·6	47·3	42·7
8·5	79·7	20·3	79·2	20·8
8·5	86·8	13·2	86·4	13·6
4·2	12·7	87·3	6·0	94·0
4·2	14·0	86·0	5·5	94·5
4·2	17·1	82·9	9·6	90·4
4·2	26·9	73·1	16·0	84·0
4·2	41·0	59·0	19·0	81·0
4·2	56·4	43·6	28·1	71·9
4·2	76·7	23·3	46·3	53·7
4·2	80·1	19·9	47·5	52·5
4·2	83·9	16·1	49·2	50·8
4·2	85·3	14·7	52·0	48·0
4·2	91·5	8·5	64·9	35·1
4·2	93·7	6·3	67·5	32·5
4·2	96·3	3·7	80·9	19·1
3·3	20·4	79·6	7·1	92·9

continued on the following page

TABLE XXVIII (continued)

Pb/(Na + Ca) in atoms	Ca at.-%	Na at.-%	$CaCl_2$ mol.-%	NaCl mol.-%
3·3	21·9	78·1	9·0	91·0
3·3	49·3	50·7	21·9	78·1
3·3	66·1	33·9	30·9	69·1
3·3	67·4	32·6	32·0	68·0
3·3	72·9	27·1	37·7	62·3
3·3	84·3	15·7	48·0	52·0
3·3	96·2	3·8	72·9	27·1
2·1	23·1	76·9	5·9	94·1
2·1	28·9	71·1	8·8	91·2
2·1	32·4	67·6	11·3	88·7
2·1	70·0	30·0	30·9	69·1
2·1	78·1	21·9	38·1	61·9
2·1	79·0	21·0	37·0	63·0
2·1	80·2	18·8	38·8	61·2
2·1	90·0	10·0	49·8	50·2
2·1	90·0	10·0	52·0	48·0

TABLE XXIX. - EQUILIBRIUM: $Ca + 2NaCl \rightleftharpoons CaCl_2 + 2Na$ (800°C.)
WITH THE ADDITION OF ANTIMONY TO THE METAL PHASE

Sb/(Na + Ca) in atoms	Ca at.-%	Na at.-%	$CaCl_2$ mol.-%	NaCl mol.-%
39·3	2·9	97·1	7·6	92·4
	10·3	89·7	25·2	74·8
	12·1	87·9	24·0	76·0
	20·2	79·8	39·3	60·7
	24·6	75·4	44·0	56·0
	36·6	63·4	57·5	42·5
	49·2	50·8	66·0	34·0
	64·7	35·3	82·0	18·0
	70·6	29·4	82·8	17·2
	87·0	13·0	93·2	6·8

between sodium and calcium and their chlorides in the fused state, preferred to start with calcium and sodium chloride. The calcium metal was fractionally distilled under reduced pressure and freed from nitride and oxide; calcium chloride was dehydrated by heating at 850°C. in hydrogen chloride, sodium chloride by fusing in a platinum crucible; pure commercial sodium was used without further purification. The reactants were heated in a steel tube provided with a welded lid.

After being chilled, the metallic phase was treated first with alcohol and then with warm water, and the milky liquid analyzed for total alkalinity and calcium.

The salt phase contains small amounts of sodium and calcium which are determined.

Rinck's results, which are different from those of Lorentz and Winzer, are given in detail in Table XXX.

In Fig. 9 the concentration of calcium chloride in the salt phase is plotted against total concentration of calcium in the metal phase, and the isotherms represent equilibria where a change in the composition of the salt phase produces a change in that of the metal phase. At the points *a*, *b*, *c*, *d* a new metallic phase appears, *i.e.* a saturated solution of sodium in calcium; as long as the two metallic phases co-exist, the concentration of the salt phase remains constant. If calcium is added to the system the respective points are

TABLE XXX. - EQUILIBRIUM REACTION IN THE FUSED STATE

$2NaCl + Ca \rightleftharpoons CaCl_2 + 2Na$

Temp. °C.	Initial state mol. ratio Ca/NaCl	Final state			
		Metallic phase		Salt phase	
		at.-% Ca	at.-% Na	mol.-% $CaCl_2$	mol.-% NaCl
712	0·365	2·63	97·37	44·0	56·0
	0·438	3·75	96·25	51·8	48·2
	0·467	10·7	89·3	53·4	46·6
850	0·244	2·47	97·53	25·5	74·5
	0·292	4·12	95·88	34·0	66·0
	0·365	5·93	94·07	41·3	58·7
	0·438	6·30	93·70	51·4	48·6
	0·438	6·67	93·33	51·5	48·5
	0·511	14·4	85·6	54·0	46·0
	0·511	16·2	83·8	55·2	44·8
	0·584	18·7	81·3	56·4	43·6
	0·584	20·0	80·0	55·8	44·2
	0·656	25·8	74·2	56·1	43·9
	0·730	29·0	71·0	55·1	44·9
	0·730	31·5	68·5	55·9	44·1
	0·730	31·8	68·2	55·1	44·9
	0·730	34·1	65·8	55·0	45·0
	0·904	39·8	60·2	53·2	46·8
	1·094	51·0	49·0	55·1	44·9
	1·459	56·2	43·8	54·4	45·6
	2·291	71·1	28·9	55·5	44·5
	3·005	76·9	23·1	60·3	39·7
975	0·365	6·73	93·27	38·9	61·1
	0·438	8·20	91·80	47·6	52·4
	0·511	10·5	89·5	52·9	47·1
	0·511	12·5	87·5	53·2	46·8
	0·554	19·8	80·2	53·7	46·3
	0·730	27·6	72·4	54·1	45·9
	0·730	31·5	68·5	55·1	44·9
	0·730	32·3	67·7	53·8	46·2
	1·312	53·1	46·9	54·6	45·4
	1·459	60·2	39·8	57·7	42·3
	1·604	63·2	36·8	59·1	42·3
	2·189	65·6	34·4	62·0	37·1
	2·920	75·2	24·8	65·4	34·6
1100	0·438	8·92	91·08	41·9	58·1
	0·481	12·2	87·8	46·5	53·5
	0·511	13·9	86·1	51·3	48·7
	0·511	15·7	84·3	53·2	46·8
	0·584	21·3	78·7	54·3	45·7
	0·730	28·4	71·6	56·5	43·5
	0·730	30·8	69·2	55·1	44·9
	0·875	35·5	64·5	55·0	45·0
	1·094	43·6	56·4	57·8	42·2
	1·240	49·5	50·5	59·6	40·4
	1·312	52·5	47·5	60·9	39·1
	1·459	56·2	43·8	60·0	40·0
	1·941	62·9	37·1	63·6	36·4

continued on the following page

TABLE XXX (continued)

Temp. °C.	Initial state mol. ratio Ca/NaCl			Final state			
				Metallic phase		Salt phase	
				at.-% Ca	at.-% Na	mol.-% $CaCl_2$	mol.-% NaCl
	Ternary mixtures						
	Ca	Na	NaCl				
850	0·025	0·087	0·12	1·26	98·74	15·8	84·2
	0·025	0·074	0·0855	3·53	96·47	28·6	71·4
	Ca	$CaCl_2$	NaCl				
850	0·10	0·065	0·076	75·3	24·7	60·8	39·2
	0·10	0·090	0·041	84·5	15·5	66·9	33·1
	0·10	0·094	0·0342	93·2	6·80	75·6	24·4
	0·065	0·126	0·0171	96·88	3·12	87·4	12·6
975	0·10	0·07	0·076	70·0	30·0	63·3	36·7
	0·10	0·093	0·038	87·3	12·7	73·8	26·2
	0·10	0·094	0·034	91·2	8·8	76·2	23·8
1100	0·10	0·066	0·076	54·9	45·1	59·8	40·2
	0·10	0·095	0·038	87·0	13·0	77·2	22·8

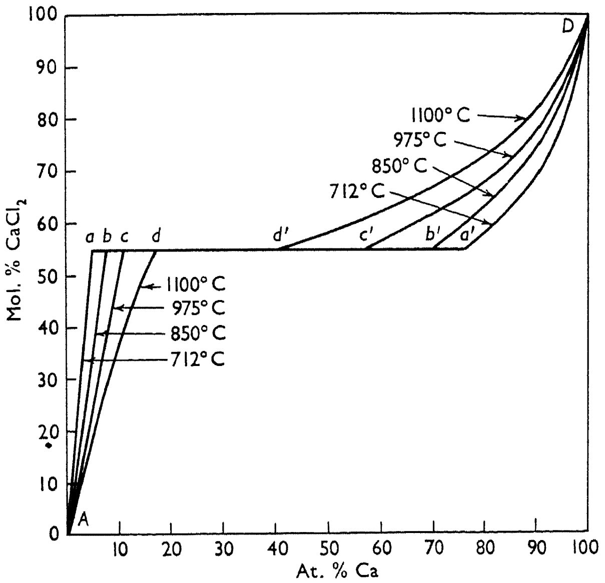

FIG. 9. ISOTHERMS OF THE REACTION: $2NaCl + Ca \rightleftharpoons CaCl_2 + 2Na$

displaced towards a^1, b^1, c^1, d^1 on a line parallel to the abscissae, and at a_1, b_1, c_1, d_1 the light metal phase disappears. The composition of the metal phase at the points of change in variance indicates the solubility of one metal in the other at the temperature of the isotherm.

As long as the molecular ratio of Ca/NaCl is not greater than 0·44, the metallic phase is a solution of calcium in sodium; the solubility of calcium increases with increase in temperature whereas the concentration of calcium chloride in the salt phase decreases. A rise in temperature thus favours the formation of calcium and sodium chloride: $2Na + CaCl_2 \rightarrow 2NaCl + Ca$ and the reaction takes place with evolution of heat. At high temperatures calcium dissolves in sodium with absorption of heat and sodium dissolves in calcium with evolution of heat. A mixture of sodium and calcium chlorides rich in the latter dissolves calcium chloride with absorption of heat whereas a mixture poor in calcium chloride gives out heat when calcium chloride is dissolved in it. The composition of this system at various temperatures is given in Table XXXI.

TABLE XXXI. - COMPOSITION OF THE MONOVARIANT SYSTEM $Na/Ca/NaCl/CaCl_2$

Temp. °C.	Composition of monovariant system					
	Salt phase		Heavy metal phase		Light metal phase	
	mol.-% $CaCl_2$	mol.-% NaCl	at.-% Ca	at.-% Na	at.-% Ca	at.-% Na
712	55	45	77·0	23·0	4·0	96·0
850	55	45	71·0	29·0	7·26	92·74
975	55	45	56·2	43·8	10·85	89·15
1100	55	45	39·3	60·7	16·5	85·5

The solidification diagram for calcium–sodium alloys has been prepared by Rinck.[233]

Equilibria of the type: $2Na + MCl_2 \rightleftharpoons 2NaCl + M$, where M is calcium, strontium or barium, have been studied by Jellinek and Czerwinski.[237,247] An electrolytic method has been used, molten lead serving as the cathode and a carbon rod as anode. Salt mixtures of definite composition were fused above the lead and the operation temperature was about 1000°C. The equilibria conform to the law of mass action and the temperature coefficients of the equilibria studied are exceptionally small. Whereas in aqueous solution at room temperature the sequence of the normal potential of the metals is: lithium, potassium, barium, strontium, sodium, calcium and the difference over the range from lithium to calcium is 0·5V., the sequence at 1200°C. in fused chlorides is potassium, sodium, lithium, barium, strontium and calcium and the difference between the potentials of potassium and calcium at 300°C. is only 0·04V. In Fig. 10 equilibria in the systems $2Na + MCl_2 \rightleftharpoons 2NaCl + M$ and $Na + MCl \rightleftharpoons NaCl + M$ at about 1000°C. are illustrated by plotting at.-% of M in sodium (no account being taken of the lead present) against mol.-% of MCl_2 or MCl in sodium chloride in the original salt mixture.

The theory of equilibrium between metals and salts in fused melts has been discussed by Lorentz.[248] The equations deduced are essentially modifications of the mass action law for condensed systems and the constants calculated for various equilibrium conditions, which include the work of Jellinek and Czerwinski on equilibria of the type $2Na + MCl_2 \rightleftharpoons 2NaCl + M$ where M is calcium, strontium or barium, agree fairly well with experimental values.

Sodium reacts with calcium chloride in an atmosphere of hydrogen according to the equations: (*a*) $2Na + H_2 \rightarrow 2NaH$; (*b*) $2NaH + CaCl_2 \rightarrow CaH_2 + 2NaCl$. The temperature for reaction (*b*) must be above the dissociation temperature of sodium hydride but below the fusion temperature of the charge.[249]

Metallic calcium and/or calcium hydride are obtained by reduction of anhydrous calcium chloride with sodium in the presence of hydrogen.[250]

The equilibrium between sodium and aluminium and their chlorides or fluorides in the fused state closely follows the ideal mass action law. In the system, $3NaCl + Al \rightleftharpoons 3Na + AlCl_3$, the equilibrium between 800° and 900°C. is strongly displaced towards the left and only 0·002 to 0·005% sodium is found in the metal phase and only 0·003 to 0·02% aluminium in the salt phase. The equilibrium constant for $[Na]^3[Al^{+++}]$ is $5{\cdot}2 \times 10^{-10}$ at 825°C. and $5{\cdot}8 \times$

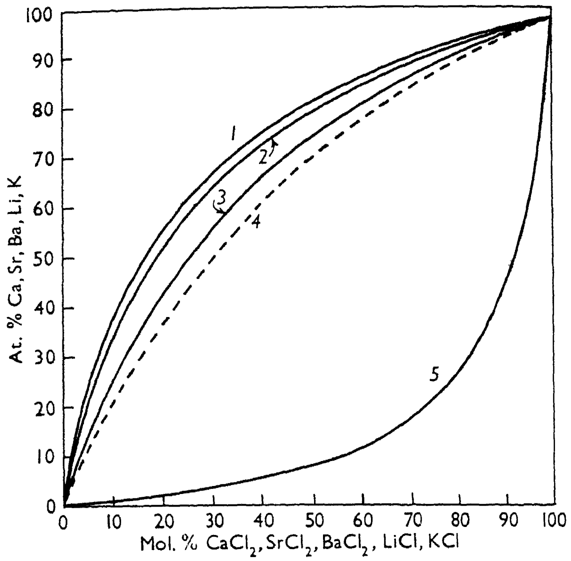

FIG. 10. EQUILIBRIA: $2Na + MCl_2 \rightleftharpoons 2NaCl + M$

10^{-10} at 900°C. In the reaction, $3NaF + Al \rightleftharpoons 3Na + AlF_3$, the equilibrium is displaced a little more to the right at 1090° C. than in the chloride system, probably because aluminium is more strongly bound in the complex $[AlF_6]'''$ than in $[AlCl_4]'$. The amount of sodium in the metal phase is 0·004%, 0·01% and 0·1% when the amount of aluminium in the fluoride slag is >12·8%, <12·8% and 1% respectively. From the equilibrium constants above and below 12·8% Al, the dissociation of the $(AlF_6)'''$ complex can be determined. In a pure cryolite melt at 1090° C. the dissociation of the complex $(AlF_6)'''$ is 1–2%.[251]

Above 1090°C. the reaction $AlF_3 + 3Na \rightleftharpoons 3NaF + Al$ proceeds from right to left and sodium is produced. Under reduced pressure sodium can be obtained at a lower temperature. This reverse reaction is used to improve 12% eutectic aluminium alloys in which sodium, liberated from sodium fluoride, refines the silicon grains.[227]

The equilibrium $Na + KCN \rightleftharpoons K + NaCN$ has been investigated by Lemke.[252] The apparatus is such that a central partition in the container divides it into two compartments of which one (*A*) contains fused potassium chloride and the other (*B*) fused sodium cyanide. Molten sodium is added and floats on the surface of the salts and the addition of sodium is continued until the layer of sodium rises to a level above the central partition to form a 'bridge' between the two fused salts. At (*A*) potassium is extracted from potassium chloride and is replaced by an equivalent amount of sodium. The potassium rapidly diffuses through the metal layer to the cyanide side where it displaces an equivalent amount of sodium from sodium cyanide to form potassium cyanide. The process continues until chemical equilibrium is reached. The resulting potassium cyanide–sodium cyanide may be caused to react with a fresh batch of potassium chloride in a second stage of the process and similarly the chloride melt may react with fresh sodium cyanide. By varying the number of stages the composition of the cyanide and chloride melts can be controlled, or the control may be effected by varying the ratio of potassium chloride to sodium cyanide fed to the apparatus. This technique can be used in other applications provided that the salts melt at a temperature below the b.p. of the alkali metals and that the anions are not reduced by alkali metals. Thus the above double countercurrent extraction may be applied to the exchange of alkali metals between hydroxides, bromides, iodides, chlorides and cyanides.

Experimental values for the equilibrium constant [Na][KCN]/[K][NaCN] = 8·7 at 680° where the quantities in brackets represent mole-% of the respective salts in the salt phase and of the respective metals in the metal phase. From this result and the equilibrium constants given by Rinck for the reactions KCl + Na $\rightleftharpoons$ K + NaCl and KOH + Na $\rightleftharpoons$ K + NaOH the equilibrium constants for the reactions NaCN + KCl $\rightleftharpoons$ KCN + NaCl and NaCN + KOH $\rightleftharpoons$ KCN + NaCH have been calculated.

The reduction of titanium tetrachloride to titanium by the sodium process is now carried out on a commercial scale, and metallic titanium, which withstands severe corrosive conditions and is resistant to seawater attack, is now available as also are its alloys, which have the strength of high tensile alloy steel with only half its weight and withstand high temperatures better than other light metal alloys.

The literature contains many references to this reaction particularly in patents, and these are here briefly outlined.

Most of the processes described, some of which are continuous,[253-309] refer to the reduction by sodium metal of the tetrachloride but the other halides, excepting the fluoride, may also be used. In one example excess of titanium tetrachloride is reduced with sodium and the products, titanium, sodium chloride and excess titanium tetrachloride are leached with water containing an oxidant, such as nitric acid, to retard adsorption of hydrogen on the washed titanium product.[253] Reduction of the tetrachloride, bromide or iodide may be effected by metallic sodium in the presence of zinc or cadmium; free titanium is obtained by distilling off the alloying metal from the molten titanium-zinc or titanium-cadmium alloy.[262] Reduction may be carried out in the liquid or vapour phase using atomized liquid sodium in an inert atmosphere; ductile titanium is produced.[263] A review of the literature up to 1955 is given by Kroll[310] and an account of the early history of titanium and its production by the sodium process by Hunter.[311]

The molar free energy, ΔG(g.-cal.) for the reaction: $TiCl_4 + 4Na \rightleftharpoons Ti + 4NaCl$ is $-226{,}200 + 65{\cdot}2T$.[312] A review of the thermodynamics of the reaction is given by Sergeev.[313] Equilibria in fused salts containing titanium tetrachloride and alkali metal have been studied by Resnick and Hornstein[314] and the conditions necessary for the formation of titanium investigated.

Titanium tetrachloride has also been reduced to titanium by sodium-potassium alloy,[315] by high surface sodium adsorbed on an inert carrier such as sodium chloride[64] and by sodium amalgam.[316-324]

Titanium or zirconium tetrachlorides are reduced by a continuous method to the subhalides by heating with 1–3 equivalents of sodium at a temperature between the fusion point of sodium and that of the sodium chloride.[309]

The additive compounds obtained when the chlorides of titanium, nickel, chromium, boron, aluminium, silicon, vanadium, manganese and beryllium are treated with ammonia or organic bases are reduced with sodium amalgam to the metal. The amalgam may be obtained in the reduction process by adding for example mercury during the electrolysis of a molten mixture of alkali halide and aluminium chloride. The amalgam formed reacts with the residual aluminium chloride to give aluminium.[327]

Titanium tetrachloride is reduced by sodium in liquid ammonia solution to metallic titanium, identified by electron diffraction; complex titanium salts containing nitrogen are also formed: TiNCl, NaNTiNH and $Na[Ti(NH)_2]$. Titanium cannot be separated from these complexes by ordinary methods. The existence of a sodium complex has also been noted in the product formed by electrolyzing a solution of sodium chloride in liquid ammonia while adding titanium tetrachloride.[326]

The refractory metals zirconium, hafnium, thorium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten and uranium are produced in a pure crystalline form by the reduction of a halide, preferably a chloride, with sodium amalgam. The metals are not appreciably soluble in mercury nor do they form stable compounds with mercury; up to 1000° C. they are not appreciably soluble in sodium chloride produced in the reaction.[320] Other information concerning the reduction of zirconium halide by sodium amalgam has been recorded.[324]

Ruthenium trichloride when titrated with sodium amalgam in dilute acid solution is reduced and the following colour changes observed: red-brown to sepia-brown and then to the blue of the monovalent ruthenium ion, Ru^+. In strong acid solution the production of a green colour marks the end-point of the titration of Ru^{+++} to Ru^{++} and the colour is said to be due to the presence of an addition product with the strong concentration of acid. Further addition of amalgam gives the blue colour of Ru^+. The reduction may be carried further to give ruthenium metal.[325]

Beryllium, chromium and zirconium are formed in a granular state, and uranium and vanadium as metallic powders, when the corresponding pure anhydrous chlorides are reduced with sodium. The yields are: beryllium, 30%; chromium, 57%; uranium from its pentachloride, 94%. Vanadium tetrachloride is somewhat difficult to reduce and large pressures are developed in the bomb, but the trichloride is readily reduced giving a 93% yield of vanadium; only a 63% yield is obtained from the tetrachloride. Zirconium from zirconium chloride is produced in a 76% yield and from potassium zirconium fluoride in a 96–97% yield.[328]

The reduction of beryllium chloride with sodium in an inert gas atmosphere[329] is described also by Kroll[227] who stresses the need for a fully deoxidized bath; an oxidized beryllium chloride bath produces fine metal crystals, more susceptible to attack by water when the reaction product is leached, especially in the presence of chloride ions. Beryllium chloride dissolved in sodium chloride, to reduce evaporation losses of the former, reacts with sodium in the presence of aluminium, preferably in an inert atmosphere, to form alloys of aluminium with up to 10% beryllium.[227]

A stable complex, beryllium fluoride-sodium fluoride, is formed by the action of sodium on beryllium fluoride. Only a part of the beryllium in the fluoride is obtained as metal: $2BeF_2 + 2Na \rightleftharpoons BeF_2{,}2NaF + Be$.[227]

Improved processes and apparatus are described for the preparation of zirconium by the reduction of its halides (except the fluoride) with molten sodium at 750°-1000° C. in an inert molten halide bath.[254]

Part of the magnesium used for the reduction of zirconium tetrachloride can be replaced by sodium. Cast iron is better as a constructional material than mild steel when used in contact with hot zirconium; a layer of zirconium carbide is formed by diffusion of zirconium and decreases contamination of the product with iron. Gaseous zirconium tetrachloride is piped to the crucible and the reaction salts repeatedly tapped to make room for more reducing metal.[330]

Zirconium, hafnium, niobium, molybdenum, tantalum and tungsten chlorides are converted to the metal by heating with sodium in a closed reactor at 750° to 1450° C. The reactor is cooled externally so that the walls are below the melting point of the halide of the reducing metal. Sodium is charged and sodium chloride removed continuously to maintain a constant level of molten salt in the reactor. The metals, zirconium and hafnium are withdrawn in the form of a solidified sponge.[260,261]

The separation of tantalum and niobium from their ores involves reduction by sodium of the tantalum and niobium double fluorides formed in one stage of the process.[331] The reduction of a fluoroniobate with sodium to produce niobium is described by Kalchin and Sumarovka.[332]

Zirconium tetrachloride in the liquid or vapour phase is allowed to react with atomized liquid sodium in an inert gas and the rate of addition of the reactants is such that sodium is present in excess of the stoicheiometric proportion.[263] Other processes for reducing the volatile halides of zirconium and hafnium with sodium have been described.[260,261,333]

One of the drawbacks involved in the substitution of magnesium for clean oxide-free sodium for the reduction of zirconium tetrachloride to zirconium is that leaching of the sponge is risky on account of the explosion hazard when more or less finely divided zirconium is brought into contact with water. This is confirmed by recent accidents. Vacuum distillation at an elevated temperature to separate the sodium chloride from the sponge introduces a fire hazard because of thin crusts of pyrophoric sodium, condensed in the cooler parts of the retort, and of the pyrophoric properties of zirconium itself.[227] Accounts of the production of zirconium by reduction of the tetrachloride with sodium are given by Miller[303] by Lustman and Kerze[334] and by Hohn *et al.*[290] In the reduction of zirconium tetrachloride with sodium an important step in the process is the removal of oxide formed by the hydrolysis of the chloride on exposure to moisture. This is effected by resubliming the chloride shortly before the reduction stage. The reduction of an alkali fluozirconate with sodium to produce zirconium powder is carried out as follows. An aqueous solution of zirconyl chloride is converted to tetrafluoride by treatment with hydrogen fluoride, an appropriate amount of potassium fluoride is added and the solution evaporated until the compound K_2ZrF_6 crystallizes. The salt is filtered off, dried and mixed with 10% excess of sodium and loaded into a bomb which is heated to 1000°-1200° C. Excess sodium is disposed of by treatment with alcohol, the zirconium metal powder is leached with water and sodium hydroxide solution, and then with hydrochloric acid, and finally washed with water and dried.

The corrosion resistance of zirconium to sodium is sensitive to the oxide content of the zirconium.

Zirconium metal has also been produced by first reducing the tetra- or trihalide to the divalent halide by liquid sodium amalgam; the halide is then decomposed and hydrogenated. The metal is obtained from the hydride.[319]

Zirconium chloride is reduced smoothly, rapidly and at relatively low temperatures with high-surface sodium adsorbed on a solid inert carrier. The metal produced is of colloidal dimensions, extremely reactive, pyrophoric when exposed to air, and should be used as formed in a continuous or semi-continuous process.[64]

For the reduction of chromium chloride, solid particles are introduced beneath the surface of a liquid pool of a 0·9% sodium amalgam. The amalgam is maintained at 200° C. in an atmosphere of helium and is vigorously agitated. The reaction mass is removed from the surface of the liquid amalgam and heated to volatilize the mercury. The remaining mixture contains metallic chromium in an amount approximately 90% of the chromium content of the chromium chloride originally present.[320]

Cuprous and nickel chlorides are reduced readily by high surface sodium adsorbed on the inert solid carrier, sodium chloride; yields of 80-90% of copper and nickel are obtained at reduction temperatures of 275° C. and 200° to 250° C. respectively.[64]

The halides of iron, copper, zinc, silver, chromium, cobalt, cadmium, tin, manganese, nickel and molybdenum are reduced to pyrophoric metal powders when treated with sodium dispersed in toluene or ether. The optimum reaction temperature for iron chloride is 30° C. and for copper, zinc and chromium chlorides, 85° C. Excess sodium in the reaction mixture is removed by extraction with *iso*propyl alcohol and the metal powders are dried in an inert gas such as nitrogen. Alloy metal powders are made in a similar manner from the appropriate halide salt mixtures.[335,336]

Metal halides are reduced to metal powders by the highly coloured addition compounds formed when sodium metal is added to polynuclear hydrocarbons in 'active ether' media such as 1:2-dimethoxyethane and dimethyl ether. Sodium reacts with naphthalene in 1:2-dimethoxyethane to form a dark green solution which contains the sodium addition compound of naphthalene of empirical formula $C_{10}H_8Na_2$. If nickel chloride is added to this solution, finely divided nickel powder is obtained of an average particle size of less than 20 microns. Iron, cobalt and other metal powders may be obtained in the same way.[337] Ferrous chloride, obtained by almost completely dehydrating ferrous sulphate heptahydrate from nickel waste liquors and treating with hydrogen chloride at 10°-65° C., is converted into high-purity iron by allowing a saturated solution of the chloride to react with sodium amalgams. The last traces of mercury are removed by heating. A completely closed mercury, sodium and chloride cycle is maintained in the continuous process.[338]

Atomic reactions of sodium with volatile polyhalides have been investigated by Heller and Polanyi by the diffusion flame method. In the reaction between sodium vapour and titanium tetrachloride, the partial pressure of sodium is about 3×10^{-3}mm.Hg, that of the inert carrier gas 1–10mm. and the temperature of the reaction about 270° C. Reaction occurs with a noticeable amount of inertia and is sometimes accompanied by a faint bluish glow. The reaction velocity constant k is based on the relation:

$$k = \frac{(\ln p_{Na}/p_0 - \ln R/r)^2}{(R-r)^2} \cdot \frac{\delta}{p_{(\text{halide})}} \cdot \frac{1}{T}$$

where p_{Na}, p_0 are the partial pressures of sodium at the centre and edge of the flame respectively, p_0 being 10^{-5}mm., R and r the radius of the flame and nozzle respectively (r = 0·25cm.), δ the diffusion constant of sodium vapour in the carrier gas, $p_{(\text{halide})}$ the partial pressure of the halide gas in the reaction chamber and T the absolute temperature. The reaction velocity constant is 993 $\text{c.c.mole}^{-1}\text{sec.}^{-1} \times 10^{-11}$ and the collision number 6·4.[158] The calculated heat of activation is 1 kg.-cal.[115]

The reaction with germanium tetrachloride is practically instantaneous and is accompanied by a blue luminescence which is brought about by reaction (*b*): (*a*) $Na + GeCl_4 \rightarrow NaCl + GeCl_3$; (*b*) $GeCl_3 + GeCl_3 \rightarrow GeCl_4 + GeCl_2 + h\nu$. The reaction velocity constant is $4890 \text{c.c.mole}^{-1}\text{sec.}^{-1} \times 10^{-11}$ and the collision number 1·3.

The reaction with mercuric chloride has been studied by the highly dilute flame method described previously (see page 450).[92,95-97,105,106,339-343] The reactions which occur are: $Na + HgCl_2 \rightarrow NaCl + HgCl + 25$ kg.-cal.; $Na + HgCl \rightarrow NaCl^* + Hg + 65{\cdot}3$ kg.-cal. (secondary reaction); $NaCl^* + Na \rightarrow NaCl + Na^*$: $Na^* \rightarrow Na + h\nu$. The luminescence is associated with the secondary reaction but is weaker than that produced with the halogens and sodium vapour. The calculated heat of activation is zero.[115]

Similar reactions occur with sodium vapour and mercuric bromide and iodide.[94,343] The primary reaction with mercuric bromide is: $Na + HgBr_2 \rightarrow NaBr + HgBr$; the secondary reaction: $Na + HgBr \rightarrow NaBr + Hg$. The total heat evolved is 86 kg.-cal.

The reaction between sodium vapour and cupric chloride or cupric bromide vapour has been studied by the method of highly dilute flames at 300°C. An intense surface light and a feeble space light are observed, the spectrum of the space light showing little else than the *D* line of sodium. The colour of the surface light for the reaction $CuCl_2$ + Na is bluish-green whereas that for $CuBr_2$ + Na is blue or bluish-violet. The spectrum for the first reaction is almost completely in the region of the cuprous chloride spectrum and that for the second reaction in the cuprous bromide region. The reactions: $CuCl_2$ + Na → NaCl + CuCl and $CuBr_2$ + Na → NaCl + CuBr are believed to be wall reactions giving solid sodium chloride and gaseous cuprous halide.[339]

The light- and precipitation-curves for the reactions between sodium vapour and the halides of cadmium and zinc chloride, carried out by the highly dilute flame method, are of the same type as for the mercury halides. Every collision results in reaction: Na + $CdCl_2$ → NaCl + CdCl (primary reaction); Na + CdCl → NaCl + Cd (secondary reaction). The light yields for the flame at the nozzle are much smaller than for mercuric chloride, 11%, and decrease in the order: cadmium chloride, 1·5%, bromide, 1%, iodide, 0·8%, zinc chloride, about 0·2%. Raising the temperature of the reaction zone does not affect the light emission.[343,344]

Sodium vapour at 0·01mm. pressure has been brought into contact with the vapours of tin tetrachloride, tetrabromide and tetraiodide. With an excess of the halide, reduction to the dihalide occurs and there is no deposit of tin on the walls of the vessel. The chloride gives a blue light, the bromide a green one and the iodide a yellow colour. The luminescence is intense and continuous.[345] Heller and Polanyi have studied the reaction of tin tetrachloride with sodium vapour by the highly dilute flame method and found it to be practically instantaneous and accompanied by a blue luminescence. The primary reaction is: Na + $SnCl_4$ → NaCl + $SnCl_3$; the secondary reaction: $SnCl_3$ + $SnCl_3$ → $SnCl_4$ + $SnCl_2$ + $h\nu$ which brings about the luminescence. The reaction velocity constant obtained when sodium vapour at a pressure of about 3×10^{-3}mm.Hg is allowed to react with the vapour of tin tetrachloride in an inert gas atmosphere at 1–10mm. pressure at 270°C. is 3510c.c.mol.$^{-1}$sec.$^{-1}$ $\times 10^{-11}$ and the collision number 1·8.[158,346] The heat of activation for the above reaction is zero.[115]

Violent reaction occurs when sodium is heated with vanadium oxychloride, $VOCl_3$, at 180°C.[347]

Mixtures of sodium with certain halides explode when subjected to mechanical shock as indicated in Table XXXII.[112]

No reaction occurs between sodium and the following halides when mixtures are subjected to shock: sodium, magnesium, calcium, strontium, barium halides; silver chloride, bromide, iodide, zinc fluoride and bromide, manganese fluoride and iodide and the complex, UCl_4,2KCl.

Anhydrous sodium fluotitanate, added to molten sodium in the ratio of four equivalents of sodium to one mole of the fluotitanate, is reduced to titanium by heating in an inert atmosphere at 500° to 1300°C.[348]

There is no appreciable reaction between sodium and sodium tungstate, Na_2WO_4, at 900°C. When mixtures of sodium with sodium tungstates, formed by heating the compound, Na_2WO_4 with different proportions of tungsten oxide, WO_3, were heated at 900°C., the yield of tungsten was in the following order according to the proportion of oxide used: $5NaO_2,12WO_3 > Na_2W_2O_7 > Na_2WO_4$. It is concluded that the reactions are: WO_3 + 6Na → $3Na_2O$ + W and $3Na_2O$ + $3WO_3$ → $3Na_2WO_4$, *i.e.* $4WO_3$ + 6Na → $3Na_2WO_4$ + W; the reaction is irreversible.[349] Sodium diffusion in sodium tungsten bronzes has been measured in single crystals of the substance $Na_{0.78}WO_3$ at 664°, 752° and 832°C. The data obtained from several crystals held at constant temperature for varying periods give a family of curves showing the sodium concentration as a function of depth and time. From these curves the mass of sodium transferred through a plane parallel to the surface and at any particular depth can be obtained. The slope of this curve divided by the concentration gradient, both evaluated at the same time and depth, is taken as the diffusivity for the corresponding concentration.

TABLE XXXII. - EFFECT OF SHOCK ON MIXTURES OF SODIUM AND HALIDES

Halide	Type of explosion	Halide	Type of explosion	Halide	Type of explosion
CCl_4	Very violent	IBr	Strong	SBr_2	Strong
PCl_5	Very violent	BBr_3	Strong	$CrCl_4$	Strong
PBr_3	Very violent	AlF_3	Strong	$MnCl_2$	Strong
SCl_2	Very violent	$AlCl_3$	Strong	$FeCl_2$	Strong
$FeCl_3$	Very violent	$AlBr_3$	Strong	NH_4Br	Weak
$FeBr_3$	Very violent	ThBr	Strong	NH_4I	Weak
$FeBr_2$	Very violent	$SiCl_4$	Strong	$CuBr_2$	Weak
FeI_2	Very violent	$SnCl_2$	Strong	CuCl	Weak
$CoCl_2$	Very violent	$SnCl_4$	Strong	CuBr	Weak
$CoBr_2$	Very violent	SnI_4 + S	Strong	CuI	Weak
$CuCl_2$	Strong	$AsCl_3$	Strong	ZnI_2	Weak
$CuCl_2.2NH_4Cl$	Strong	AsI_3	Strong	CdF_2	Weak
AgF	Strong	$SbCl_3$	Strong	$CdCl_2$	Weak
$ZnBr_2$	Strong	$SbBr_3$	Strong	$CdBr_2$	Weak
HgF_2	Strong	SbI_3	Strong	CdI_2	Weak
$HgCl_2$	Strong	$BiCl_3$	Strong	I_2	Weak
$HgBr_2$	Strong	$BiBr_3$	Strong	ThCl	Weak
HgI_2	Strong	BrI_3	Strong	CrF_3	Weak
HgCl	Strong	VCl_5	Strong	$MnBr_2$	Weak
-		-		NiF_2	Weak
-		-		$NiCl_2$	Weak
-		-		$NiBr_2$	Weak
-		-		NiI_2	Weak

The diffusivity of sodium in $Na_{0.78}WO_3$ is represented by the equation $D = D_0 \exp(-\Delta H/RT)$ where $D_0 = 0{\cdot}87$ sq. cm./sec. and $\Delta H = 51{\cdot}8$ kg.-cal./mole. For $Na_{0.8}WO_3$ the length L at temperature T_c is given by $L = L_0[1 + (8{\cdot}81 \times 10^{-6})T_c - (1{\cdot}92 \times 10^{-9})T_c^2]$, where L_0 is the length at 0°C.[350] The electrical properties of the sodium tungsten bronzes have been tabulated by Juretschke.[351]

Silicon tetrachloride is reduced to silicon, smoothly, rapidly and at relatively low temperatures, 160° to 220° C., by sodium dispersed on sodium chloride as an inert carrier.[64]

Reduction of silicon tetrachloride with sodium yields silicon containing 2 p.p.m. of boron.[269] For producing high purity silicon this process is more economical than hydrogen reduction or reduction of silicon monoxide.[352] Lower halides and mixed halides of Group IVb, Vb and VIb elements and silicon are obtained by gas phase reduction of higher halides with insufficient sodium for complete reduction. They may be further reduced if required.[353] When monochlorosilane, SiH_3Cl, is shaken for 16hr. with sodium amalgam (1g. of sodium in 10c.c. of mercury) a mixture of hydrogen and silane, SiH_4, but no silicoethane, Si_2H_6, is obtained. The reaction is considered to be:· $2SiH_3Cl + 2Na \rightarrow Si_2H_6 + 2NaCl$, the silicoethane decomposing with sodium as it is formed to give hydrogen and silane. Silicoethane in the nascent state reacts more rapidly with sodium than in the molecular form. Dichlorosilane reacts with sodium amalgam to give hydrogen and silane; no unchanged dichlorosilane remains.[354]

Atomic reactions of sodium with the halides of boron and silicon and the oxychloride of chromium have been studied by the diffusion flame method at low pressures and in the presence of an inert carrier gas at 270°C. The partial pressure of sodium vapour is about 3×10^{-3}mm. and that of the carrier gas 1-10 mm. Boron trichloride and silicon tetrachloride show the greatest inertia. No luminescence is observed in the reaction with silicon tetrachloride; with silicon tetrabromide a yellow luminescence occurs, with boron trichloride a grey luminescence, with boron tribromide a blue luminescence and with chromium oxychloride a much more intense light of a blue-green colour accompanies the reaction. With all but silicon tetrachloride, a continuous spectrum is observed. Table XXXIII gives the reaction velocity constants and the collision numbers.[153]

TABLE XXXIII. - ATOMIC REACTIONS OF SODIUM WITH THE HALIDES OF BORON AND SILICON AND THE OXYCHLORIDE OF CHROMIUM

Halide	Reaction velocity constant (k) c.c.mole^{-1}sec.$^{-1}$ × 10^{-11}	Collision no.
$SiCl_4$	4·03	1570·0
$SiBr_4$	1450·0	4·4
BCl_3	4·71	1350·0
BBr_3	248·0	25·6
CrO_2Cl_2	1330·0	4·8

Boron trifluoride is reduced to boron by reduction with sodium. Sodium vapour, diluted with helium, is passed into a reactor into which boron trifluoride is introduced separately. The mixture is heated to start the reaction which is then self-maintained at about 1500°C. Crystalline boron is obtained. The most suitable material for the reactor is boron carbide, B_4C, which withstands the high temperature and is inert to boron. Liquid sodium may be sprayed into the reactor instead of using sodium vapour.[355]

Sodium and hydrogen react with boron trifluoride: $4Na + 2H_2 + BF_3 \rightarrow NaBH_4 + 3NaF$; $6Na + 3H_2 + 2BF_3 \rightarrow B_2H_6 + 6NaF$. The molten alkali metal is atomized into a current of dry hydrogen supplied under pressure and heated to avoid chilling the metal and to accelerate the reaction. Sodium hydride is formed with liberation of heat and reacts with the boron-containing compound. The reaction temperature is adjusted to 150°–350°C. The reaction products are passed into a closed collecting chamber; the solid products settle to the bottom while the gaseous products such as boranes and excess hydrogen are withdrawn for appropriate recovery. Other reactions which may be brought about in this way are: $12Na + 6H_2 + 3BF_3 + AlCl_3 \rightarrow Al(BH_4)_3 + 12NaF$; $9Na + 3BF_3 + 3NH_3 \xrightarrow{H_2} B_3N_3H_6 + 9NaF + 1{\cdot}5H_2$. The metallic borohydrides are excellent reducing agents and provide efficient sources of hydrogen.[356]

Boron trichloride is reduced to crystalline boron by the action of dispersed sodium.[355] The heat of formation, ΔH, and free energy, ΔF° for the reaction: $3Na(c) + BCl_3(g) \rightarrow 3NaCl(c) + B(c)$ are −200·2 and −184·45kg.-cal. respectively at 298°K.[33]

Boron chloride, fluoride or bromide reacts with hydrogen at 200°-400°C. in the presence of an alkali metal, an alkali earth metal, magnesium, aluminium or zinc to give boron hydrides. A diluting gas, e.g. argon, helium or nitrogen, may be mixed with the halide and hydrogen. An example is given using granular aluminium, but the aluminium may be replaced by molten sodium. The products are condensed at −190°C. and distilled.[357]

Sodium, hydrogen and methyl borate, $B(OCH_3)_3$, under pressure at 250°C. give mainly the compound $NaBH(OCH_3)_3$ and small amounts of sodium borohydride, $NaBH_4$.[358] Sodium borohydride is, however, produced in almost quantitative yield by agitating molten sodium with a high shear in a refined high boiling mineral oil, heating in a hydrogen atmosphere and adding methyl borate to the finely dispersed sodium hydride. The sodium borohydride is extracted with a solvent and dried. Sodium methoxide is also formed. The sodium dispersion technique has several advantages; the rate of hydride formation is faster and the oily coating makes it easier to handle; the reaction of methyl borate with sodium hydride formed in this way is ten times faster, it does not require excess hydride and proceeds efficiently. The oil absorbs the heats of solution and reaction thus preventing decomposition which might result from over-heating.[65] In the rapid reaction between sodium hydride and methyl borate at 225°–275° C. to produce sodium borohydride (which is extracted in almost quantitative yield with *iso*propylamine) ethyl and butyl borates and $NaB(OCH_3)_3$ and $NaB(OCH_3)_4$ can be substituted for methyl borate.[358]

The reaction: $4Na + 2H_2 + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$ is carried out as described above for the reaction with boron trifluoride.

The action of sodium amalgam on boron hydrides causes condensations and not removal of hydrogen as with silicon hydrides.[359]

Molten aluminium chloride monoammine reacts with sodium to give hydrogen: $AlCl_3NH_3 + 3Na \rightarrow AlCl_3Na_3N + 1{\cdot}5H_2$. The liberation of hydrogen is probably due to the changed inner structure of the NH_3 molecule when present in the molecule $AlCl_3,NH_3$.[360]

In a study of electrolytic conduction processes in glass using electric light bulbs suspended in electrolytes of sodium chloride, sodium bichromate solutions and fused sodium nitrate–sodium nitrite mixtures, the lamp filament being used as the cathode, the sodium of the glass was more or less replaced by the anion of the electrolyte.[361]

The action of sodium on evacuated Pyrex vessels for a prolonged time is only slight at 230°C. but at 350° to 400°C. the glass becomes dark brown in colour and on cooling the sodium appears to crystallize inside the glass. The brown product is slightly soluble in alcohol and readily soluble in water. The weight of glass dissolved by sodium after heating *in vacuo* for 7hr. at 350°C. is about 0·005g. per 14·4g. of glass.[362]

When finely ground Thüringian glass is shaken with a sodium–silver nitrate melt for 4hr. at 380°C., the displacement of sodium by silver in the glass rises rapidly to over 90%, when the melt contains 20mole-% of silver. With pure silver nitrate, all the sodium is replaced by silver. No appreciable amount of sodium is displaced when the glass is treated in a silver bromide bath.[363]

Sodium-resistant glass, suitable for electrical discharge work, contains about 30%B_2O_3, not more than 50%SiO_2 nor more than 0·1% of iron oxide, with alkalis, alkali earths and aluminium oxide.[364] Other compositions given are: 50–75%B_2O_3, 3–15%SiO_2 and less than 10% of alkali metal oxide; or 25–30% BaO, 50–20%B_2O_3 and less than about 20%SiO_2.[365]

A glass resistant to metal vapours such as sodium, and suitable for alkali metal lamps, contains 10–40% of boric acid, 10–35% of alumina, a total of not more than 5% of tetravalent oxides and oxides of antimony, arsenic, lead and alkali metals and 25–80% of bivalent oxides (but not more than 5% of zinc oxide); the sum of 1½ times the percentage of bivalent oxides plus the percentage of alumina equals at least 45%.[366]

Other references have been made to rendering glass resistant to attack by sodium vapour.[367-372]

The rate of penetration of the reaction of a molten metal such as sodium into a vitreous or an agglomerated oxide, such as SiO_2, is determined by the temperature and the ratio of $B{:}A$ where A and B are the molecular volumes of the initial oxide and the reaction product respectively at the temperature of the reaction. When B/A is greater than 1, as in Table XXXIV, the reaction soon stops because of the formation of a protective layer; when B/A is less than 1 the protecting layer contains fissures that permit further attack on the oxide by the molten metal.

TABLE XXXIV. - REACTION OF SODIUM WITH SILICA

Solid phase	Liquid phase	Products		Temp. °C.	A	B	B/A
		Insoluble	Soluble				
SiO_2 (glass)	Na	Na_2O	Si	250	27·2	55·2	2·03
		Na_2SiO_3				34·4	1·26

The attack of sodium on vitreous silica at 250° C. is superficial.[373]

Sodium can be stored for long periods at room temperature in 2–3mm. glass tubing about 50cm. long. The sodium is melted and driven into the tubes; only the open end is subject to oxidation. The end section is broken off and discarded and short lengths of the tube are added directly to a reactor.[374]

The efficiency of the dealkalization of glass surfaces has been determined by the use of radioactive sodium. Glass specimens have been irradiated with deuterons to change some of the ^{23}Na isotope in the glass to the radioactive isotope ^{24}Na. When heated in contact with a dealkalizing agent (clay or chromium trioxide), some of the radioactive sodium is transferred from the glass to the agent. The agent is scraped from the glass surface after cooling and from the composition and distribution of induced radioactive sodium the efficiency of the agent can be determined.[375] The appearance, chemical constitution, hardness and electrical conductivity of non-metallic materials containing silica, such as glasses and ceramics, can be altered without changing their form or size by heating to 700°–900° C. in contact with reducing metals such as sodium for a sufficient time to transform *in situ* a substantial part of the siliceous material to one with a metallic appearance. Particles of sodium oxide are embedded in a matrix of an alloy of the metal with silicon.[376] In an investigation of the structural effects on colours in glass, Cole[377] suggests that alkali metals can assume a covalency of four in glasses by accepting co-ordinate links from lone pairs of electrons from oxygen in the silicon network. The experimental work on amber coloured glass shows that with constant amounts of colouring additions, iron oxide, sulphur and carbon, the depth of colour is increased when silica is replaced by soda in a base glass composition. The deepening of colour is assumed to occur by a process analogous to reduction and that with the exception of the special effect of zinc oxide, the colour becomes paler by an oxidation effect. The alkali metals arranged in order of increasing reducing power *i.e.* increased basicity are: potassium, sodium, lithium.

Polythene can be used as a casing material for sodium; no reaction occurs and the metal does not adhere to the polythene.[378]

Sodium metal aids the bonding of Teflon. After solvent cleaning, Teflon is dipped into a 1% solution of metallic sodium in liquid anhydrous ammonia for a few seconds, then quenched in water and allowed to stand in air. It can then be cemented to aluminium, mild steel, wood or Teflon with conventional adhesives.[379]

Good resistance to corrosion by sodium liquid or vapour at 900° C. is shown by molybdenum, tungsten, tantalum, synthetic sapphire, single-crystal magnesium oxide, molybdenum silicide, $MOSi_2$, and sintered thoria. Good resistance to corrosion by sodium after 100 hours at 1500° C. is shown by molybdenum wire.[380]

The corrosive resistance of various metals and alloys in sodium is illustrated by bar graphs which indicate approximate temperatures below which static and dynamic systems might be operated for 1000hr. with less than 0·005 in. of attack or container surface removal. For temperatures below 1500° F., the austentitic (300 series) stainless steels are the most satisfactory materials. Oxygen is the most troublesome impurity and should be avoided if mass transfer is to be minimized. Nickel-base alloys such as Inconel (approximately 77%Ni, 15%Cr, 7%Fe) suffer temperature-gradient mass transfer in dynamic sodium systems above 1400° F. The metal crystals deposited in the cold sections contain approximately 90%Ni, 8%Cr and <0·5%Fe, which indicates the preferential transfer of nickel by sodium. The precious metals have very poor resistance to liquid alkali metals even at moderately low temperatures. Carbon is readily transferred between two metals of different carbon content when in contact with sodium, or a monometallic system may be carburized owing to a high carbon concentration in the sodium. The walls of a stainless steel capsule in contact with sodium intentionally contaminated with carbon for 100hr. at 1500°F. were heavily carburized to a depth of 15mils. Contamination of sodium by various hydrocarbons may also result in subsequent carburization of metal containers.[33,381,382] Numerous other authors refer to corrosion by liquid sodium.[383-404]

Problems associated with the use of sodium as a coolant such as corrosion, mass transfer, diffusion bonding, induced activity, preferential attack of certain materials, blockage by oxides and the effects of oxygen on the behaviour of materials have been discussed by Brush and Koenig.[405] A preliminary study has been made of the fatigue of stainless steel in contact with liquid sodium at 300°C.[406]

Sodium reacts with oxygen-containing salts such as nitrates, sulphates, hydroxides, chromates, manganates, silicates but not with sodium carbonate or sodium monoxide. It is inert to molten baths of its halides, amide, cyanide and hydride.[143] Silicates, alkaline earth sulphates and lead sulphate are decomposed by sodium at a dull red heat.[207]

Chemical reactions with alkali metals, such as the removal of water or hydroxylated organic compounds from liquids, are exemplified by the use of molten sodium to remove small amounts of *iso*butyl alcohol from *iso*butyl vinyl ether.[408]

Alkali metal dispersions, which are stable against settling and agglomeration and in which the dispersed metal does not exceed 50μ in size, are prepared in an inert liquid hydrocarbon having a boiling point above the melting point of the metal, and in the presence of an emulsifying agent, such as 1:10-dimethoxy-3:7-decadiene. Under suitable conditions this process is said to give a stable dispersion in which the average size of the sodium particles is 8μ. The unusually finely divided form of the metal may be used as additives for Diesel fuels of inferior ignition characteristics to increase the cetane number of the fuel. Compounds suitable as emulsifying agents are complex addition compounds of the type (*a*) alkali metal alkoxides of the general formula, MOR, where M is an alkali metal and R an aliphatic, *cyclo*aliphatic or aromatic radical or (*b*) alkali metal organic compounds in which an alkali metal atom is directly attached to an allylic residue, *i.e.* compounds with at least one residue of the structure C:CCM where M represents an alkali metal. The addition compounds of either type in which the ratio of total carbon atoms to total alkali metals is 2–7:1 are preferred.[409]

Alkali metal vapours may be separated from gases by absorption in molten tin distributed as discrete drops throughout a mass of granular refractory material, such as a mixture of 120g. of 30-mesh tin and 480g. of 40-mesh silicon carbide.[410]

The handling of sodium, the hazards and precautions necessary in working with sodium are described by a number of workers.[33,91,382,411-413]

Other references to the chemistry and industrial uses of sodium are given.[414-418]

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REACTIONS OF SODIUM IN LIQUID AMMONIA

A. Inorganic Reactions in Liquid Ammonia.

The oxidation of sodium in liquid ammonia has been investigated by several workers. Kraus and Whyter passed a controlled stream of oxygen through a solution of the metal at liquid ammonia temperatures and measured the volume of oxygen absorbed and the weights of the products formed. On slow oxidation, sodium hydroxide and sodium amide are formed: $2Na + 0{\cdot}5O_2 \rightarrow Na_2O$; $Na_2O + NH_3 \rightarrow NaOH + NaNH_2$. On further oxidation the amide is oxidized to sodium nitrite: $2NaNH_2 + 1{\cdot}5O_2 \rightarrow NaOH + NaNO_2$. On rapid oxidation sodium peroxide is produced and is stable in liquid ammonia. No evidence of the formation of a higher oxide is obtained, contrary to the observations of Joannis[2] who claimed to have obtained an oxide Na_2O_3. The product, Na_2O,NH_3, found by Joannis, is considered by Kraus and Whyte to be a mixture of sodium hydroxide and amide.

Evidence for the existence of sodium superoxide, NaO_2, in liquid ammonia is given by Schechter, Sisler and Kleinberg.[3] Oxygen is passed at a rate of about 900cm.^{3}/min. through solutions of sodium in liquid ammonia at -77°C. and the volumes of gas absorbed and liberated from the solid residue are given in Table XXXV.

It is highly probable that sodium superoxide is formed at -77°C., the small amount of oxygen liberated from the solid residue being no doubt due to the instability of this oxide. The residue before analysis was obviously heterogeneous and appeared to be a mixture of yellow and white substances. If the reaction is so controlled that the blue colour of a solution of sodium in liquid ammonia is not formed, the product obtained by the rapid oxidation of sodium corresponds to the formula $NaO_{1{\cdot}67}$ *i.e.*, $Na_2O_2,4NaO_2$. The presence of sodium superoxide is confirmed by magnetic measurements. The uncontrolled reaction produces some sodium nitrite by oxidation of the amide.[4,5]

The solutions of sodium superoxide in liquid ammonia are yellow and some

TABLE XXXV. - ABSORPTION OF OXYGEN BY SODIUM IN LIQUID AMMONIA AT -77° C.

Na g.	Dilution cm.^{3}NH$_3$/g.Na	% Theoretical uptake of O$_2$	% Theoretical liberation of O$_2$
0·02	380	90	56
0·0616	680	86	50
0·0183	1200	90	54
0·0293	1830	87	56
0·0191	2490	90	50

yellow matter is suspended in them. After removal of the solid matter, absorption studies show a maximum on the absorption curve at about 380mμ due to the presence of the superoxide which is less soluble than the lithium oxide but more so than potassium superoxide.[6]

Sodium superoxide is soluble to the extent of about 0·3g. in 100cm.^{3} of liquid ammonia and undergoes some decomposition when stirred in this medium.[7]

The action of ozone on solutions of sodium in liquid ammonia at -70°C. probably results in the formation of ozonide but the compound is too unstable to permit isolation and analysis. A gelatinous white mass of the hydroxide is first formed, the blue colour of the metal solution disappears, the hydroxide dissolves and a deep orange solution and a precipitate are formed. The readiness of formation and the stability increase in the order, sodium, potassium, rubidium and caesium. Much nitrate is also formed.[8]

Sulphur reacts very readily with solutions of sodium in liquid ammonia at -33° C. A white, apparently amorphous precipitate of the monosulphide is first formed, followed by further reaction with sulphur to give light yellow or orange disulphides. These in turn are converted into readily soluble tetrasulphides which form orange-yellow solutions. The following reactions occur: $2Na + S \rightarrow Na_2S$; $Na_2S + S \rightarrow Na_2S_2$; $Na_2S_2 + 2S \rightarrow Na_2S_4$; $Na_2S_4 + (x - 4)S \rightarrow Na_2S_x$.[9] Sodium monosulphide, which is white, becomes coloured on exposure to moist air.[10]

The results shown in Table XXXVI have been obtained by potentiometrically titrating a suspension of pure sulphur in liquid ammonia, to which sodium iodide is added to increase the conductivity of the solution, with a liquid ammonia solution of sodium.

TABLE XXXVI. - POTENTIOMETRIC TITRATION OF SULPHUR IN LIQUID AMMONIA WITH A LIQUID AMMONIA SOLUTION OF SODIUM

Temp. °C.	Contents of reaction vessel	In burette	Point of inflexion ml.	Composition of compound
-60	369·1mg.S + 200mg.NaI in 80ml.NH$_3$	578·0mg.Na in 74·18ml. NH$_3$	10·34 13·39 16·69 65·79	Na_2S_6 Na_2S_5 Na_2S_4 Na_2S
-61	63·1mg.S + 200 mg.NaI in 70 ml.NH$_3$	102·7mg.Na in 74·03ml. NH$_3$	10·88 15·95 22·35 30·68 65·54	Na_2S_6 Na_2S_4 Na_2S_3 Na_2S_2 Na_2S
-60	47·2mg.S + 200mg.NaI in 70ml.NH$_3$	73·8mg.Na in 75·43ml. NH$_3$	9·90 11·51 13·83 16·82 68·00	Na_2S_7 Na_2S_6 Na_2S_5 Na_2S_4 Na_2S

Solutions of the sulphur-rich polysulphides are an intense red colour, and as the titration proceeds they become light yellow, finally yielding a white precipitate of sodium monosulphide. It is only at certain concentrations that the compounds Na_2S_7, Na_2S_5 and Na_2S_3 are formed.[11]

The preparation of sodium monosulphide from its elements in liquid ammonia is also described by Klemm, Sodomann and Langmesser.[12]

Potentiometric titrations of liquid ammonia solutions of the alkali polysulphides with liquid ammonia solutions of the alkali metals have been conducted at -38° C. by Watt and Otto. In the case of sodium, salts of the type Na_2S_4 and Na_2S are formed.[13]

Selenium reacts very readily with liquid ammonia solutions of sodium at -33° C. to give initially a white, sparingly soluble and apparently amorphous precipitate of the monoselenide: $2Na + Se \rightarrow Na_2Se$. Further reaction with excess of selenium gives di- and poly-selenides.[9,10,12]

The results given in Table XXXVII are obtained by potentiometric titrations of a suspension of selenium in liquid ammonia, containing sodium iodide to increase the conductivity of the solution, with a solution of sodium in liquid ammonia.[11]

TABLE XXXVII.- POTENTIOMETRIC TITRATIONS OF SELENIUM IN LIQUID AMMONIA WITH A SOLUTION OF SODIUM IN LIQUID AMMONIA

Temp. °C.	In reaction vessel	In burette	Point of inflexion ml.	Composition of compound
-60·0	104·8mg. Se + 200 mg. NaI in 75ml. NH_3	70·8mg. Na in 74·03ml. NH_3	12·48 16·07 21·59 32·07 63·89	Na_2Se_5 Na_2Se_4 Na_2Se_3 Na_2Se_2 Na_2Se
-60·0	32·52mg. Se + 200 mg. NaI in 80ml. NH_3	20·12mg. Na in 75·93ml. NH_3	11·56 – 18·20 24·20 35·80 72·34	Na_2Se_6 Na_2Se_5 Na_2Se_4 Na_2Se_3 Na_2Se_2 Na_2Se

Tellurium reacts vigorously with a solution of sodium dissolved in liquid ammonia; a white crystalline precipitate of the normal telluride, Na_2Te, is formed and when all the sodium is used up the solution is yellow. With excess of tellurium higher tellurides are formed.[10,12,14,15]

The reaction between sodium and tellurium in liquid ammonia has also been studied by potentiometric titrations of a suspension of tellurium in liquid ammonia, containing sodium iodide to increase the conductivity of the solution, with a sodium solution. Typical results are given in Table XXXVIII.[11]

The heat of formation of the tellurides, Na_2Te and $NaTe$, measured by Kraus and Ridderhof by determining the heat of reaction and of solution in liquid ammonia at -34° C., is 28·1 and 25·4kg.-cal./g.-atom respectively.[16]

Polyarsenides, as well as the normal arsenide Na_3As, are formed when a solution of sodium in liquid ammonia is allowed to react with freshly sublimed arsenic: $3Na + xAs \rightarrow Na_3As_x$.[17]

Potentiometric titrations of elementary arsenic in liquid ammonia with a solution of sodium in the same solvent give no evidence of compound formation. If, however, a solution of sodium in liquid ammonia is titrated with a liquid ammonia solution of arsenic trisulphide, points of inflexion occur indicating the formation of compounds, as shown in Table XXXIX.

The first compound, Na_3As, is formed as a brown precipitate and the solution

TABLE XXXVIII. - POTENTIOMETRIC TITRATIONS OF TELLURIUM WITH SODIUM IN LIQUID AMMONIA

Temp. °C.	In reaction vessel	In burette	Point of inflexion ml.	Composition of compound
-54·5	187·2mg.Te + 200 mg.NaI in 77·98 ml.NH_3	74·9mg.Na in 77·98 ml.NH_3	19·43 23·33 35·04 71·44	Na_2Te_4 Na_2Te_3 Na_2Te_2 Na_2Te
-60·7	235·4mg.Te + 200 mg.NaI in 60ml. NH_3	94·6mg.Na in 79·18 ml.NH_3	22·17 35·08 69·51	Na_2Te_3 Na_2Te_2 Na_2Te

TABLE XXXIX. - POTENTIOMETRIC TITRATIONS OF SODIUM AND ARSENIC TRISULPHIDE IN LIQUID AMMONIA

Temp. °C.	In reaction vessel	In burette	Point of inflexion ml.	Composition of compound
-50·0	61·9mg.Na in 70 ml.NH_3	123·8mg.As_2S_3 in 80·44ml. NH_3	35·48 54·37 59·23 62·49	Na_3As Na_3As_3 Na_3As_5 Na_3As_7

becomes yellow. As higher polyarsenides are produced the colour of the solution becomes a dark, reddish brown. The presence of sodium sulphide formed in the reaction: $(6x + 6)Na + xAs_2S_3 \rightarrow 2Na_3As_x + 3x\,Na_2S$. produces turbidity.[11]

Gaseous arsine passed into a liquid ammonia solution of sodium at -78° C. reacts very rapidly, changing the colour of the sodium solution from blue to green and finally to a brilliant yellow colour. The disappearance of the blue colour indicates the completion of the reaction: $Na + AsH_3 \rightarrow NaAsH_2 + 0{\cdot}5H_2$. The dihydrogen arsenide is appreciably soluble in liquid ammonia; after removing the solvent by evaporation a pale yellow, almost white, solid remains as crystals on the walls of the reaction vessel. The crystals do not contain ammonia of crystallization and the composition is unchanged after 60hr. *in vacuo* at room temperature.[18]

On reaction with antimony, which is insoluble, the deep blue colour of a liquid ammonia solution of sodium diminishes and a dark brown precipitate collects in the bottom of the cell, the solution finally becoming light yellow in colour. This part of the reaction is very rapid, considerable heat is evolved and the reaction is completed in an hour or two. The compound formed is Na_3Sb. A slower reaction then occurs accompanied by the production of a deep red solution and disappearance of the precipitate. A series of compounds is formed and the ratio of antimony to sodium in compounds in equilibrium with free antimony varies as a function of concentration. Two compounds at least are formed, one of which has a ratio of $Sb/Na > 2$ and one < 2. In dilute solutions the compound of low antimony content is present in relatively larger quantities. Electrolysis shows that antimony is present in solution as the anion and that more than one atom of antimony is associated with each negative charge.[19]

A satisfactory end point cannot be obtained when a liquid ammonia solution of sodium is treated with antimony tribromide; the ratio of $Na/Sb = 4{\cdot}8$ found is probably too high.[20]

The following reaction occurs when sparingly soluble red antimony trisulphide in liquid ammonia is potentiometrically titrated with a solution of sodium in the same solvent as shown in Table XL: $xSb_2S_3 + (6x + 6)Na \rightarrow 2Na_3Sb_x + 3x\,Na_2S$. Red antimony trisulphide is more reactive than the black sulphide. The trisulphide is first reduced to antimony but as the reaction is slow some

TABLE XL. - POTENTIOMETRIC TITRATIONS OF ANTIMONY TRISULPHIDE WITH SODIUM IN LIQUID AMMONIA

Temp. °C.	In reaction vessel	In burette	Point of inflexion ml.	Composition of compound
−57·5	109·2mg. Sb_2S_3 in 60ml. NH_3	98·0mg.Na in 80·99ml. NH_3	38·77 49·11 73·08	Sb Na_3Sb_3 Na_3Sb
−53·5	48·53mg. Sb_2S_3 in 60ml. NH_3	41·55mg.Na in 82·13ml. NH_3	41·13 75·73	Sb Na_3Sb

polyantimonide is formed, producing a deep red solution, before all the trisulphide disappears. The compound, Na_3Sb, is present as a greyish brown precipitate.

A higher polyantimonide, Na_3Sb_7, is obtained by extraction of sodium-antimony alloys with liquid ammonia.[11]

Extraction of a sodium-antimony alloy containing 75at.-% antimony with liquid ammonia gives a residue of antimony and a viscous dark reddish brown solution of sodium polyantimonide, Na_3Sb_7,xNH_3. On evaporation of ammonia a greyish black ammine, $Na_3Sb_7NH_3$, is obtained which is very stable at room temperature and loses ammonia only exceedingly slowly on the vacuum pump. Heating at 100° C. causes the ammonia to be given off suddenly, leaving Na_3Sb_7 which decomposes to the antimonide, NaSb, and antimony.[21]

A review of the work of Kraus and co-workers on compounds of the type, Na_2Te_x, Na_3Sb_x, and photographic plates showing the colours of liquid ammonia solutions of sodium, sodium tellurides, Na_2Te_2, Na_2Te_4 are given by Johnson and Fernelius.[22]

Bismuth reacts with sodium in liquid ammonia to give three compounds: Na_3Bi, which is black and insoluble; Na_3Bi_3, which forms a violet solution; and Na_3Bi_{5-7} which gives a brown solution.[23]

A satisfactory end point cannot be reached when a liquid ammonia solution of sodium is treated with bismuth trichloride. The ratio of Na/Bi = 3·3 in the compound isolated is probably too high.[20]

Bismuth tri-iodide reacts in liquid ammonia with sodium to give the following compounds, Na_3Bi, Na_3Bi_3 and Na_3Bi_5.[24]

The reaction: $(3x + 3)Na + xBI_3 \rightarrow Na_3Bi_x + 3x\ NaI$ occurs when a liquid ammonia solution of sodium is titrated potentiometrically with a liquid ammonia solution of bismuth iodide as shown in Table XLI.

TABLE XLI. - POTENTIOMETRIC TITRATIONS OF SODIUM AND BISMUTH IODIDE IN LIQUID AMMONIA

Temp. °C.	In reaction vessel	In burette	Point of inflexion ml.	Composition of compound
−60	22·44mg.Na in 60 ml. NH_3	207·8mg. BiI_3 in 75·97ml. NH_3	34·12 50·58 56·29 67·68	Na_3Bi Na_3Bi_3 Na_3Bi_5 Bi
−60	45·16mg.Na in 55 ml. NH_3	424·6mg. BiI_3 in 78·08ml. NH_3	34·99 51·88 69·27	Na_3Bi Na_3Bi_3 Bi

The formation of the compound, Na_3Bi_5, is dependent on the concentrations of the solutions.[11]

Sodium bismuth alloys containing 75at.-% of bismuth react very slowly with liquid ammonia and give only weakly coloured yellowish brown solutions. In order to obtain appreciable amounts of reaction products, the extraction must be prolonged for several months. The residue on removal of ammonia from the solution has a composition of $Na_3Bi_{5\cdot85}$ and is considered to be a mixture of Na_3Bi_5 and Na_3Bi_7. These compounds are unstable in the solid state, decomposing to NaBi + Bi.[21]

Bismuth oxyiodide is reduced by sodium in liquid ammonia according to the equation: $BiOI + 3Na + NH_3 \rightarrow Bi + NaI + NaOH + NaNH_2$. With an excess of sodium, bismuthides are formed.[25]

A flocculent black precipitate is formed when a solution of sodium in liquid ammonia is titrated potentiometrically with a solution of thallium iodide in the same solvent; the decolorization of the supernatant liquid coincides with the first inflexion point referred to in Table XLII.

TABLE XLII. - POTENTIOMETRIC TITRATIONS OF SODIUM WITH THALLIUM IODIDE IN LIQUID AMMONIA

Temp. °C.	In reaction vessel	In burette	Point of inflexion ml.	$NaTl_x$ x	Remarks
-65·0	27·12mg.Na in 65 ml.NH_3	428·9mg.TlI in 77·56ml. NH_3	37·08	1·11	Decolorization+ 1st inflexion
			49·28	2·23	2nd inflexion
			68·52	32·0	3rd inflexion
-50·0	39·50mg.Na in 80 ml.NH_3	650·8mg.TlI in 75·67ml. NH_3	34·59	1·11	Decolorization+ 1st inflexion
			44·40	2·04	2nd inflexion
			64·73	47·0	3rd inflexion

From the 'x' values in the 5th column of Table XLII, it appears that compounds of the composition NaTl and $NaTl_2$ are formed.[11]

On treating a liquid ammonia solution of sodium with a weighed amount of thallous iodide, a reaction occurs immediately with the formation of a metallic precipitate; the blue colour of the sodium solution disappears and a greenish-yellow solution is formed. The composition of the reaction product, which is slightly soluble in ammonia, is Na_3Tl_2.[20]

A metallic precipitate, inactive to air and water, is formed when silver cyanide or iodide is added to a solution of sodium in liquid ammonia, the silver salt being reduced to silver.[20]

No exact or reproducible point of inflexion is obtained when a solution of sodium in liquid ammonia is titrated potentiometrically with a solution of silver iodide in the same solvent. The black precipitate formed is silver.[11]

When a silver salt such as the chloride or iodide is added to a solution of sodium in ammonia, the reaction ratio of sodium to silver salt is 1·00. $Na + AgI \rightarrow NaI + Ag$. The end point, *i.e.* the disappearance of the blue colour of the sodium solution, can be judged precisely and it has been suggested that free sodium in solution can be accurately determined by adding a weighed amount of silver chloride.[26,27]

A black precipitate is formed, and the solution of sodium in liquid ammonia is decolorized, when a potentiometric titration is carried out with a liquid ammonia solution of gold iodide. A point of inflexion is obtained shortly after the solution has been decolorized; the composition of the mixture corresponds to NaAu.[11]

Cuprous iodide is reduced by sodium in liquid ammonia to free copper.[27]

A precipitate of metallic copper with perhaps a slight amount of sodium is obtained when a liquid ammonia solution of sodium is titrated potentiometrically with a solution of copper iodide in the same solvent. The supernatant liquid is decolorized. No reproducible point of inflexion is obtained.[11]

The low solubilities of cadmium iodide and cyanide in liquid ammonia are responsible for the difficulty experienced with the end point when the solution is added to a liquid ammonia solution of sodium. The ratio of Na/Cd found for the precipitate lies between 0·2 and 1·0, many values lying in the range of 0·5. In many cases unchanged salt is found with the precipitated metal at the end of the reaction. It is probable that the higher values for the ratio are correct and not improbable that the compound NaCd is formed. The precipitate is reactive towards air and water.[20]

The following reaction: $(2x + 1)Na + xCdI_2 \rightarrow NaCd_x + 2x\,NaI$ occurs when a solution of sodium in liquid ammonia is titrated with a liquid ammonia solution of cadmium iodide, potentiometrically. Points of inflexion are observed as shown in Table XLIII.

TABLE XLIII. - POTENTIOMETRIC TITRATIONS OF SODIUM WITH CADMIUM IODIDE IN LIQUID AMMONIA

Temp. °C.	In reaction vessel	In burette	Point of inflexion ml.	$NaCd_x$ x	Remarks
-55·8	25·45mg.Na in 80 ml.NH_3	238·4mg.CdI_2 in 84·17ml. NH_3	65·30	5·23	Decolorization
			66·62	6·77	1st inflexion
			69·36	16·0	2nd inflexion
			70·59	35·00	3rd inflexion
-62·3	45·17mg.Na in 80 ml.NH_3	400·0mg.CdI_2 in 72·05ml. NH_3	60·01	6·29	Decolorization + inflexion
			64·81	Cd	Inflexion

The results indicate that a phase between $NaCd_5$ and $NaCd_7$ is formed, as well as reduction of the cadmium salt to cadmium. A finely divided black precipitate is formed during the titration.[11]

An immediate reaction occurs when mercuric iodide or cyanide or mercurous iodide is added to a solution of sodium in liquid ammonia. The solution becomes colourless and the finely divided metal is precipitated. On standing, the supernatant liquid becomes blue again and the decolorization and return of the colour continue as more of the salt is added. Apparently the compound NaHg is first formed but is unstable in ammonia and breaks down to a compound richer in mercury, the freed sodium then dissolving in ammonia. By increasing the amount of salt originally added a permanently colourless solution is obtained and the precipitate has the composition $NaHg_2$.[20] The compound, NaHg, is formed when ethyl mercuric chloride is reduced by excess sodium in liquid ammonia solution.[20]

Zinc iodide and cyanide are readily reduced by sodium in liquid ammonia. Reaction occurs immediately and a finely divided metallic precipitate is formed which is extremely reactive with air and water. The ratio of sodium to zinc in the compound formed is between 0·24 and 0·289 and corresponds to the composition $NaZn_4$.[20] Burgess and Rose[28] have verified the existence of the compound $NaZn_4$ and give the following equation for the reaction: $4Zn(CN)_2 + 9Na \rightarrow NaZn_4 + 8NaCN$. A slight excess of sodium does not affect the composition of the precipitate. Oxygen is taken up rapidly by the precipitate and much heat is evolved, but the appearance of the compound is not changed. This primary oxidation is followed by a secondary reaction which proceeds at a very slow rate for a long time, the colour of the precipitate changes from black to grey and then to white. Dry air acts in the same way as dry oxygen; moist air or oxygen accelerates the reaction so that the two stages are not apparent. There is no evidence of the formation of peroxides. With dilute acid one mole of the compound $NaZn_4$ liberates nine equivalents of hydrogen, (*i.e.*, from both the sodium and the zinc present); with water, approximately 4·5 equivalents of hydrogen are liberated in two months.

Potentiometric titrations of a liquid ammonia solution of sodium with a solution of zinc iodide in the same solvent have been carried out by Zintl, Goubeau and Dullenkopf.[11] The reaction is: $(2x + 1)\mathrm{Na} + x\mathrm{ZnI_2} = \mathrm{NaZn}_x + 2x\ \mathrm{NaI}$, and details of the titration are given in Table XLIV.

TABLE XLIV. - POTENTIOMETRIC TITRATIONS OF SODIUM WITH ZINC IODIDE IN LIQUID AMMONIA

Temp. °C.	In reaction vessel	In burette	Point of inflexion ml.	NaZn_x x	Remarks
-59·5	74·43mg.Na in 60 ml.NH_3	586·9ml. ZnI_2 in 76·76ml. NH_3	66·85 68·10	11·8 22·0	Decolorization Inflexion
-55·5	35·42mg.Na in 55 ml.NH_3	270·2mg.ZnI_2 in 75·75ml. NH_3	66·33 68·15	12·8 44·0	Decolorization Inflexion

The results indicate the formation of a compound $NaZn_{12}$ or $NaZn_{13}$, but there is no evidence that the compound $NaZn_4$ is formed.

The reaction between metallic tin and a solution of sodium in liquid ammonia takes place slowly; the characteristic blue colour of the sodium solution gradually changes to greenish yellow and finally to a transparent red. The greenish yellow colour is produced no doubt by the presence of a mixture of various constituents in solution.

On adding pellets of stannous iodide to a liquid ammonia solution of sodium until a change from green to red occurs, a compound is formed in which the ratio Na/Sn is 3:8; this corresponds to the formula Na_4Sn. When an excess of stannous iodide is added, the red colour is at first intensified after which metallic tin is precipitated until the solution becomes colourless. The compound Na_4Sn is not stable in solution but breaks down giving free sodium and a compound richer in tin.[20]

Reproducible results cannot be obtained by potentiometric titration of a liquid ammonia solution of stannic sulphide or iodide with sodium in liquid ammonia solution. A deep red solution of the compound Na_4Sn_9 is formed by extracting sodium-tin alloys with liquid ammonia. Titration of this solution with a solution of sodium in the same solvent does not give satisfactory results so that it is impossible to say whether lower polystannides exist.[11]

Manganese iodide, MnI_2, is reduced by sodium in liquid ammonia solution to manganese which catalyzes the reaction between sodium and ammonia and appears to react with the sodamide formed.[27] This reaction may be used to obtain manganese for the preparation of the pure oxide by slow oxidation.[29]

Compounds of sodium with lead are formed when a liquid ammonia solution of sodium is agitated with excess lead at -33°C. They are very soluble in ammonia and separate out without ammonia of crystallization. One gram atom of sodium dissolves 2·26g.-atoms of lead and not four as indicated by the work of Joannis.[30]

In the presence of metallic lead, an equilibrium is assumed to exist between a Pb_2^- ion and another negative ion of the form Pb_3^-. The following equilibrium ratio has been calculated:-

$$(Pb_3^-)/(Pb_2^-) = 0{\cdot}26/0{\cdot}74 = 0{\cdot}36$$

(the molal concentrations of the substances refer to the conditions when 1g.-atom of sodium is present). It is assumed that there are about 3moles of $NaPb_2$ to one mole of $NaPb_3$.[31]

The addition of a lead salt to sodium in liquid ammonia results in the initial formation of the normal plumbide, Na_4Pb, but this compound is unstable and decomposes to give free sodium and a compound richer in lead. An alloy corresponding to NaPb dissolves readily in liquid ammonia to give a green solution; one corresponding in composition to $NaPb_2$ is also soluble and gives a much darker green solution; an alloy of composition Na_2Pb is slightly soluble forming a yellowish green solution.[20]

Potentiometric titrations of a liquid ammonia solution of sodium with a solution of lead iodide in the same solvent show that the following reaction occurs: $(4 + 2x)Na + xPbI_2 \rightarrow Na_4Pb_x + 2x\ NaI$. The data for typical titrations are given in Table XLV.

TABLE XLV. - POTENTIOMETRIC TITRATIONS OF SODIUM WITH LEAD IODIDE IN LIQUID AMMONIA

Temp. °C.	In reaction vessel	In burette	Point of inflexion ml.	Composition of compound
−50·2	15·48mg.Na in 75 ml.NH_3	170·1mg.PbI_2 in 69·72ml. NH_3	49·85 52·26 64·06	Na_4Pb_7 Na_4Pb_9 Pb
−50·2	102·3mg.Na in 75 ml.NH_3	1190·2mg.PbI_2 in 64·77ml. NH_3	– 45·90 55·98	– Na_4Pb_9 Pb
−50·2	271·0mg.Na in 100 ml.NH_3	2992·6mg.PbI_2 in 58·03ml. NH_3	– 43·03 52·63	– Na_4Pb_9 Pb
−50·2	54·46mg.Na in 80 ml.NH_3	622·3mg.Na in 64·24ml.NH_3	43·97 46·70 57·26	Na_4Pb_7 Na_4Pb_9 Pb

The compound, Na_4Pb_7, is not detected in the more concentrated solutions.[11]

The following reactions which occur when sodamide and amalgamated aluminium or magnesium are brought together also occur when a solution of sodium in liquid ammonia reacts with aluminium or magnesium: $Al + 3NaNH_2 \rightleftharpoons Al(NH_2)_3 + 3Na$; $Al(NH_2)_3 + NaNH_2 \rightarrow Al(NH_2)_2NHNa.NH_3$; $3Na + 3NH_3 \rightleftharpoons 3NaNH_2 + 1{\cdot}5H_2$.[32] The reaction between magnesium and liquid ammonia to form magnesium amide, $Mg(NH_2)_2$, is very slow but it is catalyzed by the presence of sodium. Sodium salts may be used in place of sodium: $2NaI + Mg \rightleftharpoons MgI_2 + 2Na$; $2Na + 2NH_3 \leftrightarrow 2NaNH_2 + H_2$; $2NaNH_2 + MgI_2 \rightarrow Mg(NH_2)_2 + 2Na$.[33]

The initial reaction between a liquid ammonia solution of sodium and a suspension of aluminium iodide hexammoniate, $[Al(NH_3)_6]I_3$ at −70°C. is rapid and attended by the immediate discharge of the blue colour of the metal solution, evolution of hydrogen and liberation of heat. The whole of the solid phase originally present at −70°C. passes into solution. The rate of reaction then falls to a very low value not greatly different from that observed for the reaction between metals and liquid ammonia. The proposed course of the reaction is: $[Al(NH_3)_6]^{+++} + NH_3 \rightarrow [Al(NH_3)_5NH_2]^{++} + NH_4^+$. This is the initial reaction. The ammonium ion is destroyed by the metal solution, ammonia and hydrogen being produced: $NH_4^+ + e^- \rightarrow NH_3 + H$. The rapid reaction continues until all the aluminium is bound in a soluble, relatively stable complex of empirical composition $Al(NH_2)_{1\cdot5}I_{1\cdot5}$. The net result is the evolution of hydrogen and the accumulation of amide in solution.[34]

Ammonium azide, NH_4N_3, with sodium in liquid ammonia forms sodium azide, ammonia and hydrogen: $Na + NH_4N_3 \rightarrow NaN_3 + NH_3 + H$. The reaction is vigorous.[35]

Refs. p. 520

Hydrogen is liberated when sodium is added to a liquid ammonia solution of ammonium bromide or iodide.[36-39] The halides behave as acids in relation to ammonia: $2NH_4Br + 2Na \rightarrow 2NaBr + 2NH_3 + H_2$; $2NH_4I + 2Na \rightarrow 2NaI + 2NH_3 + H_2$ and may be used to eliminate excess alkali metal from a reaction mixture or to reduce organic compounds *in situ*. Sodium and sodium sludges may be removed from a liquid metal system by washing with liquid ammonia and liquid ammonia-ammonium chloride.[40] The heats of reaction of the alkali metals with dilute solutions of ammonium bromide and ammonium chloride in liquid ammonia have been measured; from these values and the heats of solution of the alkali metals in liquid ammonia, the heat of reaction of each dilute solution with the ammonium ion has been found to be exothermic and within experimental error identical whether the metal be lithium, sodium, potassium or caesium, *i.e.*, a mean value of 40·4 ± 1 kg.-cal. is obtained. From the measured heats of reaction and corresponding free-energy changes, relative partial molal ionic entropies and entropies of solvation of the alkali metal ions in liquid ammonia have been calculated.[41]

The reaction between sodium and sodium nitrate in liquid ammonia has been examined, in connexion with the explosion which occurs during the electrolysis of sodium nitrate in liquid ammonia. The reaction proceeds in three stages: in the first sodium nitrite is formed, in the second the compound $Na_2N_2O_2$, caustic soda and sodamide are formed, and in the third a yellow explosive substance believed to be disodium nitrite. A similar compound is formed by the action of sodium on sodium nitrate.[42]

Sodium perchlorate and hydrogen are formed when ammonium perchlorate is added to a liquid ammonia solution of sodium; sodium iodate and periodate together with some sodium iodide and hydrogen are formed when the corresponding ammonium salts are treated in the same way.[23]

Neither sodium chlorate nor the perchlorate is reduced by sodium in liquid ammonia at -33°C., nor are they reduced by sodium and ammonium bromide in liquid ammonia.[23]

Sodium bromide, sodium hydroxide and sodamide are formed when sodium bromate is treated with sodium in liquid ammonia, the ratio $Na/NaBrO_3$ being 6/1.[23]

With sodium iodate the reaction with sodium or with sodium and ammonium bromide in liquid ammonia at -33° C. and at room temperature is very slow and incomplete, but some sodium iodide is formed.[23]

The periodate, $Na_2H_3IO_6$, is reduced to $Na_3H_2IO_6$ by sodium in liquid ammonia, while the reaction with the compound, $Na_3H_2IO_6$, is very slow and incomplete with either sodium or sodium and ammonium bromide at -33°C. in liquid ammonia; the product in the latter case is sodium iodide.[23]

There is an initial rapid reaction when potassium permanganate is treated with sodium in liquid ammonia; the products are potassium sodium manganate, $KNaMnO_4$, and manganese oxides.[23]

Sodium nitrite is reduced by sodium in liquid ammonia and a bright yellow precipitate of disodium nitrite, Na_2NO_2, is formed. This substance is very reactive towards moisture, air and carbon dioxide and explosions occur easily. In the pure state, if kept *in vacuo*, it stands moderate heating, but at 100°C. to 130°C. it decomposes violently. When treated with water it gives sodium hydroxide, sodium nitrite and sodium nitrate.[43,44]

Anhydrous nickel, cobalt and copper nitrates, manganous iodide and partially dehydrated ferric nitrate are reduced in liquid ammonia to the metal when sodium is added. With incompletely dehydrated ferric nitrate the reduction is accompanied by the formation of a complex and there is a tendency for the sodium to explode. Instead of adding the sodium piece by piece as long as the reaction proceeds, the method described for the other dehydrated materials, it is better to add ferric nitrate to sodium already dissolved in liquid ammonia when reduction proceeds smoothly. All the precipitated metals become hot enough to glow when the ammonia is removed rapidly by filtering too long on the suction pump, but if air is admitted gradually to an Erlenmeyer flask containing the metals still wet with ammonia, so that slow oxidation occurs by diffusion of air, the pure metallic oxides can be obtained. Manganese is so active that it becomes warm even while it is still wet with ammonia.[29]

The catalytic activity of nickel produced by the reduction of nickel bromide, $NiBr_2$, with liquid ammonia solutions of the alkali metals, is substantially constant per unit area for all the alkali metals. The rates of reaction are too rapid for measurement but they increase from lithium to caesium.[45]

Excess potassium tetracyanonickelate, $K_2Ni(CN)_4$, when treated with sodium in liquid ammonia, gives a bright red precipitate of potassium tricyanonickelate, $K_2Ni(CN)_3$.[46]

A lilac coloured solid, NaCO, is formed when carbon monoxide is led into a liquid ammonia solution of sodium at -50° C. At 90° C. it decomposes according to the equation: $4NaCO \rightarrow Na_2CO_3 + Na_2O + 3C$. When heated in air it explodes.[47]

The addition of ammonium chloride or hydrogen sulphide to the reaction product of sodium and carbon monoxide in liquid ammonia before evaporation of liquid ammonia, results in the formation of substances which are reasonably stable. The final product is a mixture of either the ammonium or sodium salt of rhodizonic acid, glycollic acid amide and glycollic acid. The best yields of rhodizonate and amide, based on the amount of sodium consumed, are obtained when sodium metal is added in small amounts at a time, so that it is only slightly in excess during the reaction, and when oxygen and moisture are excluded. The amide is separated from the reaction products by extraction with dioxan or ether.[48]

The following reactions occur when carbonyls are treated with a liquid ammonia solution of sodium: $[Co(CO)_4]_2 \rightarrow Na[Co(CO)_4]$; $[Fe(CO)_4]_3 \rightarrow Na_2[Fe(CO)_4]$; $Fe(CO)_5$ or $Fe_2(CO)_9 \rightarrow Na_2[Fe(CO)_4] + CO$; $[Co(CO)_3]_4 \rightarrow Na[Co(CO)_4] + Co$; $Fe(CO)_4I_2 \rightarrow Na_2[Fe(CO)_4] + NaI$. The hexacarbonyls of the chromium group and $Ni(CO)_4$ liberate carbon monoxide on reaction but the other products formed are not known.[49]

According to Evers,[50] sodium phosphide, represented empirically as Na_2P but probably present as a dimer, is formed by the reaction of the elements in liquid ammonia. Normal phosphides are not formed under these conditions.

The compound, Na_4P_2, tetrasodium diphosphide, is reduced to sodium dihydrogen phosphide when ammonium bromide is added to a solution of sodium and the tetrasodium compound in liquid ammonia: $Na_4P_2 + 2Na + 4NH_4Br \rightarrow 2NaPH_2 + 4NaBr + 4NH_3$. The formation of the PH_2 ion is shown by its conversion to CH_3PH_2, when the solution is treated with methyl iodide.[51] More recently, however, Royen and Zschaage have stated that when sodium and phosphorus react together in liquid ammonia the product is not $Na_4P_2,2NH_3$ as stated by Evers[50] but a mixture of the two compounds, $Na_2H_2P_2$ and $2NaNH_2$. The reaction with ammonium bromide is considered to be: $Na_2H_2P_2 + 2NaNH_2 + 4NH_4Br + 2Na \rightarrow 2NaPH_2 + 6NH_3 + 4NaBr$. The compound, $Na_2H_2P_2$, does not itself react with sodium.[52]

When a liquid ammonia solution of sodium and a large excess of potassium amide are allowed to stand in contact with a small quantity of platinum black, the metallic sodium is rapidly converted to sodium amide which reacts with potassium amide to form the compound, $NaNK_2,2NH_3$.

The amides of sodium and rubidium are formed separately by the action of liquid ammonia on the metals in the presence of platinum black and when rubidium amide solution is poured upon the slightly soluble sodium amide the latter dissolves forming the compound $NaNHRb,NH_3$ which is obtained in the form of beautiful crystals on concentrating the solution. A compound isolated from the mother liquor is probably dirubidium ammonosodiate, $NaNRb_2,2NH_3$.[53]

The system sodium/sodium iodide/ammonia has been studied by Sienko[54] by measuring the electrical resistance of the solution as a function of decreasing temperature. A discontinuity in the slope of the resistance-temperature curve corresponds to the temperature at which phase separation occurs. The upper critical temperature for the separation into two phases is −41·6°C.

The alkali metals react with a liquid ammonia solution of the diamnoniate of diborane, $B_2H_6,2NH_3$, and on removal of the solvent yield the alkali metal borohydride and aminoborine: $Na + B_2H_62NH_3 \rightarrow NaBH_4 + BH_2NH_2 + NH_3 + 0{\cdot}5H_2$. Sodium borohydride is soluble in ethylene glycol dimethyl ether and is separated from the reaction products by extraction with this solvent. *X*-Ray diffraction patterns have been obtained for the soluble and insoluble portions of the reaction products and the only crystalline substance is sodium borohydride in the soluble portion. The amide, BH_2NH_2, undergoes ammonolysis during the removal of the solvent ammonia, to an extent that is greatest with lithium and least with potassium.[55]

When carbon disulphide is dropped into sodium in liquid ammonia and the brown product methylated with dimethyl sulphate the following compounds are obtained: dimethyldithiondithioloxalate, $(CS_2CH_3)_2$, an isomer of this substance, the compounds $(CH_3)_2CS_3$ and $C_6H_{12}S_4$ and dimethyl sulphide.[56]

Liquid ammonia solutions of the compound BF_3,NH_3 have been titrated with solutions of sodium in the same solvent in an apparatus which permits the quantitative recovery of all the products. The following equation expresses the results obtained: $5Na + 2BF_3,NH_3 + 2NH_3 \rightarrow 5NaF + (NH_2)_2\text{-}BNHB(F)NH_2 + 2{\cdot}5H_2$.[57]

Reviews of the reactions of sodium in liquid ammonia with numerous references are given by Fernelius and Watt[58] and by Watt.[23]

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Reactions of sodium in liquid ammonia

B. Organic Reactions in Liquid Ammonia.

A review of the reactions of organic and organometallic compounds with solutions of sodium in liquid ammonia with numerous references has been given by Watt.[1]

Saturated hydrocarbons do not appear to react and in fact, reducible substances contaminating hydrocarbons may be removed by treatment with sodium in liquid ammonia.

Diphenylmethane reacts slowly at room temperature to give the sodium derivative, $(C_6H_5)_2CHNa$, in small amounts, and on oxidation this derivative yields sodium peroxide and *sym.*-tetraphenylethane; $2(C_6H_5)_2CHNa + O_2 \rightarrow Na_2O_2 + (C_6H_5)_2CHCH(C_6H_5)_2$. Triphenylmethane reacts slowly with sodium in liquid ammonia at $-33{\cdot}5^{\circ}$C. to give the sodium derivative, $(C_6H_5)_3CNa$.[1,2]

p-Benzohydryltetraphenylmethane, $(C_6H_5)_2CHC_6H_4C(C_6H_5)_3$, is stable in a liquid ammonia solution of sodium, butadiene gives butene and octadiene, whilst isoprene gives a 60% yield of 2-methyl-2-butene together with high molecular weight hydrocarbons. Alloöcimene, $(CH_3)_2C{=}CHCH{=}CHC(CH_3){=}CHCH_3$, yields 2:6-dimethyl-3:5-octadiene.[1]

The reduction of phenylated olefines has been studied by Wooster and Ryan.[3] In no case is the phenyl group attacked by the alkali metal but the double bonds in the side chain may become saturated; after decomposition of the sodium derivative with ammonium chloride, the corresponding phenylated paraffin is obtained. The stable organo-sodium derivatives react with oxygen and certain RX compounds such as ethyl bromide, dimethyl sulphate and benzyl chloride. Sodium also reacts with some of the olefines causing polymerization, dimerization, cleavage of carbon-carbon bonds and addition to but one of two double bonds in a molecule. The following reactions are described: styrene, $C_6H_5CH{=}CH_2 \rightarrow$ 50% of ethylbenzene and polymers; stilbene, $C_6H_5CH{=}CHC_6H_5 \rightarrow$ dibenzyl; *unsym.*-diphenylethylene $\rightarrow$ the sodium derivative, $(C_6H_5CNaCH_2)_2$, which is hydrolyzed by ammonium chloride to 1:1-diphenylethane and a small amount of 1:1-2:2-tetraphenyl butane, $[(C_6H_5)_2CHCH_2]_2$; triphenylethylene, $(C_6H_5)_2C{=}CHC_6H_5$, adds two atoms of sodium; tetraphenylethylene, $(C_6H_5)_2C{=}C(C_6H_5)_2$ gives a disodium compound stable in ammonia; with excess sodium and ethyl bromide, *sym.*-tetraphenylethane, $[(C_6H_5)_2CH]_2$ and diphenylethylmethane, $(C_6H_5)_2CHC_2H_5$ are formed, indicating cleavage followed by reaction with the bromide and ammonolysis; 1:1-diphenylpropene, $(C_6H_5)_2C{=}CHCH_3$ reacts readily with sodium in liquid ammonia, the primary addition product being semi-ammonolyzed; the stable products with ammonium chloride and benzyl chloride respectively are diphenylethyl ethane, $(C_6H_5)_2$-CHC_2H_5, and diphenylbenzylethylmethane, $(C_6H_5)_2C(CH_2C_6H_5)C_2H_5$. 1:1-3:3-Tetraphenylpropene, $(C_6H_5)_2C{=}CHCH(C_6H_5)_2$, reacts with two atoms of sodium and on hydrolysis with ammonium chloride forms 1:1-3:3-tetraphenylpropane; the stable red addition products with dimethyl sulphate, ethyl bromide and benzyl chloride give 1:1-3:3-tetraphenylbutane, 1:1-3:3-tetraphenylpentane and 1:1-3:3-4-pentaphenylbutane respectively. Tetraphenylpropadiene, $(C_6H_5)_2C{=}C{=}C(C_6H_5)_2$, reacts with about four atoms of sodium and on evaporation of the liquid ammonia an almost quantitative yield of 1:1-3:3-tetraphenylpropane, $(C_6H_5)_2CHCH_2CH(C_6H_5)_2$, is obtained.

Neither 1-hexene nor 2-*cyclo*propyl-1-pentene is affected by sodium in liquid ammonia, nor by sodium and ammonium bromide in the same solvent. They are, however, reduced to hexane and 2-*cyclo*propylpentane if methyl alcohol is present.[4]

Two examples are given of partial reduction of diene hydrocarbons with a conjugated double bond system by means of sodium in liquid ammonia; thus 2:4-hexadiene affords 60–65% of 2-hexene and 35–40% of 3-hexene, with about 30% of *cis* and 70% of *trans* isomers,[5] whilst 2:5-dimethyl-2:4-hexadiene gives 73% of 2:5-dimethyl-2-hexene.[6] Other similar reactions have been described by the same authors.

2:3-Dimethyl-1:3-butadiene is reduced by sodium in liquid ammonia giving chiefly 2:3-dimethyl-2-butene with a small amount of 2:3-dimethyl-1-butene. Similar reduction of 2:4-dimethyl-1:3-pentadiene yields 2:4-dimethyl-2-pentene. 2-Methyl-2:4-pentadiene gives 50% of 2-methyl-3-pentene and about 8% of material which contains some 2-methyl-2-pentene.[7]

Sodium acetylide is formed when acetylene is passed into solutions of sodium in liquid ammonia at its normal boiling point. Some of the acetylene is reduced to ethylene, but this may be avoided by adding sodium to the liquid ammonia at such a rate that there is never any appreciable excess of sodium present.[8,9]

Monoalkylacetylenes react with sodium and liquid ammonia in the following manner: $2CH_3C{\equiv}CH + 2Na \rightarrow 2CH_3C{\equiv}CNa + 2H$; $CH_3C{\equiv}CH + 2H \rightarrow CH_3CH{=}CH_2$. About two thirds is metalated and one third hydrogenated. The addition of an ammonium salt to the reaction mixture results in complete reduction and high yields of the corresponding olefines are obtained. Dialkylacetylenes on reduction with sodium in liquid ammonia give good yields of the *trans* form of the corresponding olefine. For example, reduction of 3-octyne and 4-octyne gives 98% yields of *trans*-3-octene and *trans*-4-octene respectively.[1] Attempts to reduce di*tert.*-butylacetylene to the *trans*-olefine have been unsuccessful.[10]

Diacetylenes are reduced by sodium or by sodium and ammonium sulphate in liquid ammonia to the corresponding *trans-trans* dienes; a 72% yield of 2:7-nonadiene, without evolution of hydrogen, and a 61% yield of 1:6-heptadiene are obtained from 2:7-nonadiyne and 1:6-heptadiyne respectively.[1]

Phenylacetylene is reduced by sodium in liquid ammonia to its sodium derivative and ethylbenzene: $3C_6H_5C{\equiv}CH + 4Na + 2NH_3 \rightarrow 2C_6H_5C{\equiv}CNa + C_6H_5C_2H_5 + 2NaNH_2$.[11]

The benzene nucleus is not attacked by sodium in liquid ammonia and in fact benzene, toluene and xylene may be used as solvents for reactions between sodium and many organic compounds in liquid ammonia.[1]

2:5-Dihydrotoluene is reduced to give 50% of 1-methyl*cyclo*hexene and 10% of 3-methyl*cyclo*hexene.[12] Biphenyl is reduced by sodium in liquid ammonia to tetrahydrobiphenyl[1] and at −75° C. to −70° C. to the 3:4-dihydroderivative. Further reaction with sodium yields the 3:4:5:6-tetrahydrobiphenyl. Terphenyl is reduced to a 3:4-dihydroderivative and a compound isomeric with terphenyl but containing no reactive double bond.[13]

Tetrahydronaphthalene and sodium amide are formed when naphthalene is reduced with sodium in liquid ammonia. The bright red solution formed when the reaction is carried out at −33° C. or at lower temperatures is due to the presence of an unstable intermediate compound, the 1:2:3:4-tetrasodium addition product, which is three-fourths ammonolyzed. A green colour which changes to orange-red and finally to red is produced when naphthalene is dissolved in ether and treated with sodium in liquid ammonia at −75°C. to −60° C. On treatment with methanol, Δ^2-dihydronaphthalene is formed. At the boiling point of liquid ammonia, the Δ^1-isomer is formed; at −60° C. the Δ^2-isomer in ether on treatment with sodium and liquid ammonia is converted to the Δ^1-isomer; at −50° C. it is reduced with sodium to tetralin.[1,14]

Naphthalene, sodium and *iso*butyl chloride in liquid ammonia yield 1:2:3:4-tetrahydro-1:4-di-*iso*butylnaphthalene and a little tetralin.[1,15] Anthracene is reduced by sodium in liquid ammonia to 9:10-dihydroanthracene, 9:10-diphenylanthracene to the 9:10-dialkali salt, phenanthrene to 1:2:3:4-tetrahydrophenanthrene, and dimethylfluorene to tetrahydrodimethylfluorene. Fluorene and indene give sodium salts by substitution accompanied by some hydrogenation. The addition of ammonium bromide to sodium and liquid ammonia does not cause more extensive hydrogenation of naphthalene, biphenyl, acenaphthene and phenanthrene than occurs when sodium and liquid ammonia alone are used but fluorene is more extensively hydrogenated and anthracene also, the latter yielding 1:2:3:4-tetrahydroanthracene and other products.[1]

The presence of methanol or ethanol with sodium in liquid ammonia brings about the following reactions: benzene → 1:4-dihydrobenzene, 83%[1] toluene → 2:5-dihydrotoluene, 83%[1,12] xylene (mixture) → dihydroxylenes, 87%;[1] *m*-xylene → 2:5-dihydro-*m*-xylene; p-xylene → 2:5-dihydro-p-xylene;[16] 4:5-dihydro-*m*-xylene → 1:3-dimethyl*cyclo*hexene;[12] p-cymene → γ-terpinene;[16] 1:4-dihydronaphthalene → tetrahydronaphthalene, not tetralin;[1] tetralin → 1:2:3:4:5:8-hexahydronaphthalene 91%.[1,16]

The following compounds do not react with sodium in liquid ammonia: terpinene, terpinolene, carvene, α-pinene, menthene, 1:3-dimethyl*cyclo*hexene, 2:4-dimethyl*cyclo*hexene, *D*-limonene, *D*-sylvestrene, methylgeraniolene, 4-methyl*cyclo*hexene.[1]

The halogens are usually quantitatively removed from halogen organic compounds by treatment with sodium in liquid ammonia; an analytical method is thus provided for the determination of halogens in organic compounds. The monohalogen substitution products of the paraffin hydrocarbons react to form hydrocarbons both saturated and unsaturated, sodium halides and sodium amide. A number of such reactions are given in Table XLVI taken from Watt's review.[1]

TABLE XLVI. - REACTIONS OF ALKYL HALIDES WITH SOLUTIONS OF SODIUM IN LIQUID AMMONIA

Halide	Products
CH_3Cl	CH_4, CH_3NH_2, $NaCl$
CH_3I	CH_4, CH_3NH_2, NaI
C_2H_5Br	C_2H_6, $NaNH_2$, $NaBr$
C_2H_5I	C_2H_6
C_2H_5I	C_2H_6, $C_2H_5NH_2$, NaI
C_2H_5I	C_2H_6(75%), C_2H_4(4%)
C_2H_5I	$C_2H_5NH_2$(21%), $NaNH_2$
n-C_3H_7Cl	C_3H_8, C_3H_6(trace), $NaNH_2$
n-C_3H_7I	C_3H_8
n-C_3H_7I	C_3H_8, $C_3H_7NH_2$, NaI
n-C_3H_7I	C_3H_8(71%), C_3H_6(7%), $C_3H_7NH_2$(21%), $NaNH_2$
n-C_4H_9Cl	C_4H_{10}, $NaNH_2$, $NaCl$
iso-C_4H_9Cl	C_4H_{10}, C_4H_8(trace), $NaNH_2$
iso-C_4H_9I	C_4H_{10}(70%), C_4H_8(15%), $C_4H_9NH_2$(15%), $NaNH_2$
iso-$C_5H_{11}Cl$	C_5H_{12}, C_5H_{10}(trace), $NaNH_2$
iso-$C_5H_{11}I$	C_5H_{12}, C_5H_{10}(trace), $NaNH_2$
tert.-$C_5H_{11}I$	*sec.*-C_5H_{12}(and explosion)
$C_2H_5CHI(CH_2)_2CH_3$	C_6H_{14}, C_6H_{12}(trace), $NaNH_2$
$CH_3(CH_2)_5CHICH_3$	C_8H_{18}, $NaNH_2$

The reaction of methyl iodide is complicated since it reacts with liquid ammonia forming ammonium iodide which is acted on by sodium: $4CH_3I + 4NH_3 \rightarrow (CH_3)_4NI + 3NH_4I$.

Butyl bromide reacts quantitatively with sodium in liquid ammonia and the reaction has been used to determine sodium in sodium hydride. A liquid ammonia solution of sodium is titrated with butyl bromide dissolved in *n*-hexane.[17]

meso- and *dl*-2:3-Dibromobutane with sodium in liquid ammonia yield the same mixture of *cis*- and *trans*-2-butene, but 50% *meso*- 50% *dl*- 1:2-dibromo-1:2-dideuteroethane yields slightly different mixtures of *cis*- and *trans*-1:2-dideuteroethylene. The authors discuss debrominations with sodium in liquid ammonia in terms of a free radical mechanism.[18]

Reactions of phenyl-substituted alkyl halides with sodium in liquid ammonia[1] are shown in Table XLVII.

TABLE XLVII. - REACTIONS OF PHENYL-SUBSTITUTED ALKYL HALIDES WITH SODIUM AND LIQUID AMMONIA

Halide	Products
$PhCH_2Cl$	$PhCH_3$, $PhCH_2CH_2Ph$, and a solid hydrocarbon
$PhCH_2Br$	$PhCH_2CH_2Ph$
Ph_2CHCl	$Ph_2CHCHPh_2$(66%), Ph_2CH_2(28%)
$Ph_3C.Cl$	Ph_3CNa
$PhCHCl_2$	$PhCH_2CH_2Ph$(7%), $PhCH_2NH_2$(38%)
$Ph_2C.Cl_2$	$Ph_2C{=}CPh_2$(90%)
$PhC.Cl_3$	$PhCH_2CH_2Ph$(5%), nitrogenous substance
$PhCH_2CH_2Br$	PhC_2H_5(38%), $PhCH{=}CH_2$(1·3%)
Ph_3CCH_2Cl	Ph_2CNaCH_2Ph
$Ph_3CCH_2CH_2I$	Ph_3CNa, C_2H_4
$Ph(CH_2)_3Br$	PhC_3H_7(28%), $Ph(CH_2)_3NH_2$(18%)
$Ph(CH_2)_4Br$	PhC_4H_9(43%), $Ph(CH_2)_4NH_2$(17%), other hydrocarbons and amines
$PhC(CH_3)_2CH_2Cl$	$PhC(CH_3)_3$

Acetylene dibromide yields on treatment with sodium in liquid ammonia, sodium acetylide and acetylene.[2]

The monobromo-olefines with sodium and liquid ammonia give principally the corresponding acetylenes and olefines. The acetylene/olefine ratios for 1-bromo-1-propene, 1-bromo-octene, 1,1-dibromo-1-propene and 1-1-dibromo-1-octene are 0·012, 0·45, 0·81 and 1·80 respectively.[1,19]

β-Bromostyrene in dry ether and liquid ammonia slowly treated with sodium in liquid ammonia gives 96% of phenylacetylene; α-chlorostyrene gives 15% of phenylethane; *p*-methyl-α-chlorostyrene gives 63% of tolylacetylene; stilbene dibromide with 15moles of sodium gives 73% of bibenzyl; styrene dibromide yields 66% of phenylacetylene and 2-bromo-1-decene gives 56% of 1-decene. The acetylenes prepared in this way are contaminated with hydrogenation products.[20]

The reactions of paraffin polyhalides with sodium and liquid ammonia have been summarized by Watt,[1] and are given in Table XLVIII.

TABLE XLVIII - REACTIONS OF PARAFFIN POLYHALIDES WITH SODIUM IN LIQUID AMMONIA

Halide	Products
CH_2Cl_2	CH_4(55%), $NaNH_2$, NaCl
$CHCl_3$	CH_4, $NaNH_2$, NaCl, small amounts of C_2H_4, C_2H_2, NaCN
CHI_3	CH_4, NaI, some C_2H_4, C_2H_2, NaCN, H_2 and N_2
CCl_4	CH_4, NaCl, NaCN, small amounts of N_2
CH_2ClCH_2Cl	C_2H_4, NaCl
CH_3CHCl_2	C_2H_6(51%), C_2H_4(5%), $NaNH_2$
C_2Cl_6	NaCN(not confirmed)
$CH_3CH_2CHCl_2$	C_3H_8, some C_3H_6
$CH_3CCl_2CH_3$	C_3H_8(64%), C_3H_6(14%), $NaNH_2$, NaCl
$CH_3CHBrCH_2Br$	C_3H_6, NaBr
$(CH_3)_2CBrCH_2Br$	C_4H_8, NaBr
$C(CH_2Br)_4$	$C(CH_2NH_2)_4$(small amounts)

Chlorobenzene and iodobenzene react with sodium in liquid ammonia to give benzene, diphenylamine, triphenylamine and sodium halide. A small quantity of aniline is also formed.[1]

A 50% yield of *sec.*-butylbenzene and a 10% yield of *p*-*sec.*-butylaniline are obtained when *p*-*sec.*-butylchlorobenzene is treated with sodium in liquid ammonia.[1] The following reaction occurs with *o*- and *p*-chlorotoluenes: $C_6H_4CH_3Cl + 2Na + NH_3 \rightarrow C_6H_5CH_3 + C_6H_4NH_2CH_3 + 2NaCl$.[2] A nitrogen containing residue and *o*-xylene are formed slowly when *o*-bromoxylene reacts with sodium in liquid ammonia.[1] The reaction of *o*-dichlorobenzene with sodium and liquid ammonia is as follows: $2C_6H_4Cl_2 + 4Na + 2NH_3 \rightarrow C_6H_6 + C_6H_4(NH_2)_2 + 4NaCl$.[2] α-Iodonaphthalene is reduced to naphthalene by the action of sodium in liquid ammonia. Indene bromohydrin with sodium and liquid ammonia gives a 75% yield of 2-indanol.[1]

Alkoxides are formed and hydrogen is evolved when alcohols react with sodium in liquid ammonia. Secondary and tertiary alcohols react more slowly than primary alcohols and form more soluble alkoxides. In many cases compounds of the type RONa.ROH are formed. With di- and poly-hydric alcohols, usually only one of the hydrogen atoms is replaced by sodium.

Salts of this type have been treated with alkyl halides or other alkylation agents to produce a variety of ethers.[1]

The reactions listed in Table XLIX have been described by Chablay.[21]

Many other references to similar reactions are given by Watt.[1]

Phenols react with solutions of sodium in liquid ammonia in the same way

TABLE XLIX. - REACTIONS OF ALCOHOLS WITH SODIUM IN LIQUID AMMONIA

Alcohol	Product
Methyl alcohol	CH_3ONa
Ethyl alcohol	C_2H_5ONa
*iso*Butyl alcohol	$i\text{-}C_4H_9ONa$
*iso*Amyl alcohol	$i\text{-}C_5H_{11}ONa$
Ethylene glycol	$CH_2OH\text{-}CH_2ONa$
Glycerol	Monosodium salt
Erythritol	$CH_2OH(CHOH)_2CH_2ONa$
Mannitol	$CH_2OH(CHOH)_4CH_2ONa$
Allyl alcohol	$CH_2{=}CHCH_2ONa$, C_3H_6, NaOH, NH_3
Geraniol	$C_{10}H_{17}ONa$, $C_{10}H_{18}$, NaOH, NH_3
Citronellol	$C_{10}H_{19}ONa$, H, NH_3
Linalol	$C_{10}H_{17}ONa$, $C_{10}H_{18}$, NaOH, NH_3
Cinnamic alcohol	C_9H_9ONa, $C_9H_{11}ONa$, C_9H_{10}, NaOH, NH_3

TABLE L. - REACTIONS OF PHENOLS WITH SODIUM IN LIQUID AMMONIA

Compound	Products
Phenol	C_6H_5ONa
2:4:6-Tri-*tert.*-butylphenol	Monosodium salt
Resorcinol	$C_6H_4(OH)ONa$ (very soluble) $C_6H_4(ONa)_2$
α-Naphthol	$C_{10}H_7ONa$ and traces of 5:8-dihydro-α-naphthol
β-Naphthol	$C_{10}H_{11}ONa$

as the aliphatic alcohols, but the naphthols are in part reduced to tetrahydronaphthols. Some examples are given in Table L.

Alcohols, phenols and naphthols in liquid ammonia are reduced by the hydrogen generated by the action of sodium on ethanol; e.g., benzyl alcohol yields toluene, phenylmethylcarbinol forms ethylbenzene, furfuryl alcohol gives 2:methylfuran.[1]

Aromatic ethers are acted upon by sodium in liquid ammonia according to the equation: $ROR^1 + 2Na + NH_3 \rightarrow RONa + R^1H + NaNH_2$.

The reduction of ethers by sodium and ethanol or methanol in liquid ammonia is also described by Watt; anisole gives Δ^2-*cyclo*hexenone, methylenedioxybenzene yields phenol, 3:4-methylenedioxytoluene forms p-cresol. Numerous other reactions are given with references.[1] Wooster has obtained a 60% yield of dihydroanisole from anisole, sodium and methanol in liquid ammonia.[22]

2-Methyl-2-phenyl-1:3-dioxolan and the *o*-, *m*-, p-methoxy derivatives on treatment with sodium and methanol in liquid ammonia yield ethylbenzene and the corresponding ethylanisoles which can undergo further reduction in the aromatic nucleus. 2-Methyl-2-phenyl-1:3-oxathiolan is completely hydrogenolyzed.[23]

The cleavage of diphenyl ether derivatives by sodium in liquid ammonia is described by Tomita *et al.*[24] 6:3:4-Bromomethylenedioxyphenoxybenzene, $Br(CH_2O_2)C_6H_2OC_6H_5$, in ether yields a small amount of a strong phenolic substance and a larger amount of a weak phenolic substance, $6{:}4\text{-}CH_3(HO)C_6H_3\text{-}OC_6H_5$. Excess sodium is ineffective in the cleavage of the ether linkage of diphenyl ethers. The presence of the phenolic group in *o*-, *m*- and p-hydroxyphenoxybenzene, $HOC_6H_4OC_6H_5$, hinders cleavage of the ethers with sodium in liquid ammonia. 1-Naphthyl phenyl ether and 2-naphthyl phenyl ether are cleaved by sodium in liquid ammonia into phenol and naphthalene or naphthol and benzene but 1:2-dinaphthyl ether, 1-dinaphthyl ether and 2-dinaphthyl ether give resinous substances.[25]

Most aldehydes react readily with ammonia itself. Acetals are usually unaffected by liquid ammonia or by solutions of metals in liquid ammonia.

Only a few reactions have been studied using ketones with sodium solutions in liquid ammonia. The product from acetone has not been identified; benzophenone forms a monosodium ketyl, $(C_6H_5)_2CONa$, with one equivalent of sodium and a disodium ketyl with two equivalents, $(C_6H_5)_2CNaONa$.

Benzophenoneanilide with sodium in liquid ammonia followed by treatment with ammonium bromide gives diphenylmethane and aniline.[1]

Esters react with sodium in liquid ammonia in the following way: $3RCOOR^1 + 4Na + 4NH_3 \rightarrow 2RCONH_2 + RCH_2ONa + 3R^1ONa + 2NH_3$, where $RCOOR^1$ may be ethyl acetate, methyl butyrate, methyl *iso*valerate, ethyl caproate or methyl caprylate. Esters dissolved in ethyl alcohol and treated with sodium in ammonia at -80°C. react as follows: $RCOOR^1 + 2C_2H_5OH + 4Na \rightarrow RCH_2ONa + 2C_2H_5ONa + R^1ONa$; methyl *n*-butyrate, *iso*valerate, heptylate and ethyl caproate yield butanol, *iso*amyl alcohol, heptanol and hexanol on further treatment with water.[21]

Sodium acetate does not react with sodium in liquid ammonia but sodium benzoate is reduced to sodium dihydrobenzoate; dihydro-α-naphthoic acid may be obtained by reducing the sodium salt of α-naphthoic acid with sodium in liquid ammonia.

Carbohydrates react with sodium in liquid ammonia to give sodium salts; the temperature does not appear to be critical and can, in fact, be varied from -80°C. up to room temperature. Cellulose may be converted to the mono-, di-, or tri-sodium salt, depending upon the amount of sodium used, and the salts so obtained are used to form cellulose ethers, xanthates and other derivatives. The formation of tri-sodium cellulose is catalyzed by sodium halogenides. Glucose, fructose, α-methylglucoside, glycogen, inulin, soluble starch, lichenin and chitin yield monosodium salts.[1]

The cleavage of lignin with sodium in liquid ammonia has been investigated.[26-28] Dihydroeugenol, 1-(4-hydroxy-3:5-dimethoxyphenyl) propane and lignin have been extracted from the reaction products obtained by treating aspen lignin with sodium in liquid ammonia.[26] Colourless, fibrous cellulose, dihydroeugenol and other unidentified materials have been isolated from the crude products formed by treating fir lignin with sodium in liquid ammonia.[27]

Aliphatic amines do not usually react with sodium in liquid ammonia; this solvent is not a suitable medium for reduction of the above compounds which give sodium salts readily ammonolyzed by ammonia: $RNHNa + NH_3 \rightarrow RNH_2 + NaNH_2$.

Triphenylmethylamine is converted to sodium triphenylmethide and sodium amide on treatment with sodium and liquid ammonia: $(C_6H_5)_3CNH_2 + 2Na \rightarrow (C_6H_5)_3CNa + NaNH_2$. Although aniline, ethylaniline, *o*-toluidine and diphenylamine do not react with sodium in liquid ammonia at -40°C. the monosodium salt may be formed by carrying out the reaction in an autoclave at room temperature. Slow reduction of aniline with sodium in liquid ammonia in the presence of methyl alcohol results in the formation of tetrahydroaniline; rapid reduction yields 2:5-dihydroaniline.[1]

Although methyl-2:2:6-trimethyl*cyclo*hexyl ketimine and phenyl-2:2:6-trimethyl*cyclo*hexyl ketimine are not reduced by sodium amalgam in ethyl alcohol, they are reduced with sodium in liquid ammonia yielding α-methyl-2:2:6-trimethyl*cyclo*hexanemethylamine and α-phenyl-2:2:6-trimethyl*cyclo*hexanemethylamine respectively.

The reduction of allylamines with sodium in liquid ammonia and alcohol has been studied by King.[29] *N*-Allylpiperidine is reduced to *N*-propylpiperidine; *N*-methallylpiperidine and diethylmethallylamine to the corresponding saturated compounds. The following compounds are unaffected by sodium in liquid ammonia; *N*-crotyl-, -2-*tert.*-butyallyl-, -1-*cyclo*hex-2^1-enyl-, -benzyl- and -2:3:4:5-tetrahydrobenzylpiperidine.

Acid amides react as monobasic acids with sodium in liquid ammonia to give sodium salts and hydrogen. Acetamide, propionamide, butyramide and *iso*valeramide react rapidly; part of the amide is reduced to the corresponding alkoxide. Higher homologues such as caproamide and caprylamide react slowly because of their low solubility in liquid ammonia.[21] Formamide reacts with sodium in liquid ammonia to give the sodium salt, and on further treatment with methyl methacrylate it forms monomethacrylformamide. At -33°C. benzamide is reduced to dihydrobenzamide and benzyl alcohol; sodium *N*-phenylsulphamate is converted to the disodium salt; urea and monosubstituted ureas readily form monosodium salts which are used for synthesizing substituted ureas.[1]

Amino acids are converted to their sodium salts on treatment with sodium in liquid ammonia at low temperatures. Cystine is reduced to cysteine at -33·5°C.: $S_2(CH_2CHNH_2COOH)_2 + 4Na \rightarrow 2NaSCH_2CHNH_2COONa$. Small amounts of sodium sulphide and alanine are also formed. Reactions such as these are used in the synthesis of amino acids and their derivatives; racemization does not occur and optically active derivatives of active substances may be obtained from intermediate sodium salts.[1]

The biscoclaurine alkaloids are reduced in almost quantitative yields to the optically active coclaurine bases with sodium in liquid ammonia.[30,31] The above reaction has also been applied to 3-bisbenzyl*iso*quinoline.[32] The cleavage of O-methylrepandine in toluene by sodium in liquid ammonia yields phenolic and non-phenolic bases.[33] Thebaine is reduced to dihydrothebaine-ϕ; dihydrothebaine on further reduction with sodium in liquid ammonia yields dihydrothebainone-Δ^5-enol methyl ether.[34] Pheanthine or bebeerine dimethyl ether is reduced to a non-phenolic base,[35] *l*-N-methylcoclaurine. The tosyl group in tosyl-L-glutaminyl-L-asparagine and tosyl-L-glutamine is removed with sodium in liquid ammonia. The cation-exchange resin, 'Dowex-50', is used to remove excess sodium from liquid ammonia in these reactions.[36]

α-Tolunitrile gives a sodium derivative with sodium in liquid ammonia: $C_6H_5CH_2CN + Na \rightarrow C_6H_5CHNaCN$ (or $C_6H_5CH = CNNa$) + $0{\cdot}5H_2$. Some toluene and sodium cyanide are also formed.[37]

Nitrosoguanidine yields cyanamide and nitrogen on treatment with sodium in liquid ammonia; nitrosobenzene forms disodium phenylhydroxylamine: $PhNO + 2Na \rightarrow PhNNaONa$. Nitroguanidine behaves in the same way as nitrosoguanidine but if ammonium chloride is present aminoguanidine is formed. The nitroparaffins, nitroethane, 1-nitropropane, 2-nitropropane, 1-nitrobutane and 2-nitrobutane, are slowly but incompletely reduced by sodium in liquid ammonia to alkyl hydroxylamines. The products obtained by the reduction of nitrobenzene with sodium in liquid ammonia depend upon the experimental conditions, and the following products have been reported: disodium phenylhydroxylamine, disodium anilide, (with excess sodium); azobenzene (on subsequent addition of excess ethyl bromide); azoxybenzene and azobenzene on subsequent addition of water; aniline with ammonium bromide or methanol.

A 97% yield of dihydro-1-naphthylamine is obtained by treating 1-nitronaphthalene with sodium in liquid ammonia; when the reaction is carried out using toluene as co-solvent, and in the presence of ammonium bromide, 1-naphthylamine is produced. If methanol is used in place of ammonium bromide, a mixture of di- and tetra-hydro-1-naphthylamines is formed. Tetrahydro-2-aminofluorene in 89% yield is produced when 2-nitrofluorene is treated with sodium in liquid ammonia. The addition of ammonium bromide to sodium in liquid ammonia prevents any action with 2-nitrofluorene whereas methanol added in place of ammonium bromide causes the compound to be reduced to a mixture of tetra- and hexa-hydro-2-amino fluorenes.[1]

Azoxybenzene is reduced by sodium in liquid ammonia to azobenzene which is itself reduced to the disodium salt of hydrazobenzene: $PhN = NPh + 2Na \rightarrow PhN(Na)N(Na)Ph$. Azobenzene and 2g.-atoms of sodium followed by excess of ethyl iodide yields *sym.*-diethylphenylhydrazine. With 4g.-atoms of sodium, the same product together with ethane and ethylamine is formed. Sodium in liquid ammonia with ammonium bromide reduces azobenzene to aniline. Phenylhydroxylamine is reduced to aniline with sodium and liquid ammonia. $PhNHOH + 2Na + NH_3 \rightarrow PhNH_2 + NaOH + NaNH_2$. Phenylhydrazine is reduced to its monosodium salt which reacts with alkyl halides to form alkylphenylhydrazines. A number of reactions of substituted hydrazines in liquid ammonia sodium solutions are listed by Watt,[1] and references are given. The N–N bond is ruptured by sodium and ammonium bromide in liquid ammonia; if two phenyl groups or one phenyl and another group are attached to the same nitrogen atom, the N–N bond is ruptured by sodium in liquid ammonia alone, *i.e.*, without the addition of ammonium bromide, the hydrogen liberated by replacement with sodium reducing the N–N bond.

Pyrrole is not effectively reduced by sodium and ammonium bromide in liquid ammonia. Indole is reduced to 2:3-dihydroindole, carbazole to 1:4-dihydrocarbazole. When ammonium bromide is present carbazole also forms 1:2:3:4-tetrahydrocarbazole. Sodium and liquid ammonia alone have no action on *N*-methylcarbazole, but with ammonium bromide present, dihydro-*N*-methylcarbazole is formed. The reduction of triazoles with sodium or sodium and ammonium bromide in liquid ammonia has been described in detail by Watt[1] and a number of reactions tabulated. The hydrogen displaced from 1:2:3-benzotriazole reduces the benzenoid ring, while that formed by the action of sodium and ammonium ions reduces the heterocyclic ring. Many reactions of heterocyclic compounds with liquid ammonia solutions of sodium are given by Watt.[1]

The sulphur compounds, thiourea, benzoyl sulphimide, acetone diethyl sulphone, diphenyl sulphone, dinitrophenyl thiocyanate, benzenesulphonamide, benzenesulphonyl chloride, *n*-propyl *p*-toluenesulphonate, *p*-toluenesulphonic acid and 2-naphthylamine-5:7-disulphonic acid, react with sodium in liquid ammonia to form sodium sulphide and/or sodium sulphite. After oxidizing the sodium salts with sodium peroxide, barium sulphate may be precipitated and thus a method provided for the estimation of sulphur in these compounds. Sodium mercaptides are formed by the reaction of alkylmercaptans and phenylmercaptan with sodium in liquid ammonia. An 87·5% yield of dithiopentaerythritol, $(CH_2OH)_2C(CH_2SH)_2$, is obtained by the reduction of 4:4-*bis*hydroxymethyl-1:2-dithia*cyclo*pentane with sodium in liquid ammonia. Aliphatic sulphides (such as ethyl, *n*-propyl and *n*-heptyl) react with sodium in liquid ammonia according to the equations: $R_2S + 2Na + NH_3 \rightarrow RSNa + RH + NaNH_2$ and $2R_2S + 2Na \rightarrow 2RSNa + RR$. The first reaction is the chief one. Aliphatic disulphides are reduced quantitatively to the corresponding mercaptides.

Diphenyl sulphide is reduced by sodium in liquid ammonia to benzene, sodium sulphide and a small amount of water-insoluble gas. Phenyl *iso*thiocyanate with sodium in liquid ammonia yields aniline, sodium sulphide, no cyanide and a relatively small amount of biphenyl. A 71% yield of benzene, sodium sulphite and a small amount of biphenyl have been obtained by reducing sodium benzenesulphonate with sodium in liquid ammonia. Petroleum may be purified from organic sulphur contaminants by treatment with sodium in liquid ammonia.[1]

Ethylmercuric chloride reacts with sodium in liquid ammonia according to the equation: $C_2H_5HgCl + 3Na + NH_3 \rightarrow NaCl + NaHg + C_2H_6 + NaNH_2$.[38]

Trimethylboron ammine reacts as follows: $(CH_3)_3BNH_3 + Na \rightarrow (CH_3)_3BNH_2Na + 0{\cdot}5H_2$.[39] Tetramethylboronhydride, $(CH_3)_4B_2H_2$, is split equally into the ammine of dimethylboronhydride, $(CH_3)_2BH.NH_3$, and the disodium salt, $Na_2HB(CH_3)_2$.[40]

Sodium reacts with trimethylgallium in liquid ammonia: $2(CH_3)_3GaNH_3 + Na \rightarrow [(CH_3)_3Ga]_2NH_2Na + 0{\cdot}5H_2 + NH_3$ and $2(CH_3)_3GaNH_3 + 2Na \rightarrow [(CH_3)_3Ga]Na_2 + 2NH_3$. The first reaction is the chief one, 60–100% of the total gallium reacting in this way, whereas 30–0% reacts according to the second equation.

Under similar conditions dimethylgallium chloride is reduced to dimethylgallium which combines with ammonia and may be obtained as a solid at −33°C. It decomposes slowly at this temperature, more rapidly at room temperature, to the amide: $(CH_3)_2GaNH_3 \rightarrow (CH_3)_2GaNH_2 + 0{\cdot}5H_2$. With excess sodium in liquid ammonia the ammine of dimethylgallium reacts thus: $(CH_3)_2GaNH_3 + Na \rightarrow (CH_3)_2GaNH_2Na + 0{\cdot}5H_2$.[41] Ethyl-, methyl- and *iso*amylgermane with sodium in liquid ammonia yield germanyl salts but the reactions are not quantitative.[42]

Dimethylstannyl, diphenylstannyl and diphenylgermanyl react with sodium in liquid ammonia to form the corresponding disodium salt: $(CH_3)_2SnNa_2$, Ph_2SnNa_2 and Ph_2GeNa_2.[1]

Triphenylsilane reacts with sodium in liquid ammonia to give di(triphenylsilicon)imine, $[(C_6H_5)_3Si]_2NH$.[43]

Trimethylstannyltriphenylsilane is converted to the sodium derivatives $(C_6H_5)_3SiNa$ and $(CH_3)_3SnNa$ with sodium in liquid ammonia, and trimethylstannane and triphenylstannane to their sodium salts, $(CH_3)_3SnNa$ and $(C_6H_5)_3SnNa$. The latter is converted in part to the disodium salt, $(C_6H_5)_2SnNa_2$.[1]

Triethylgermane does not appear to react with sodium in liquid ammonia but the triphenyl derivative gives the monosodium salt with some disodium salt. Methyl- and *n*-propyl-triphenylgermanes are not attacked by sodium in liquid ammonia and no appreciable reaction occurs with tetraethylgermane. Tetraphenylgermane is converted to the sodium salt by the following slow reaction: $(C_6H_5)_4Ge + 2Na + NH_3 \rightarrow (C_6H_5)_3GeNa + C_6H_6 + NaNH_2$. With excess sodium the disodium salt, $(C_6H_5)_2GeNa_2$, is formed. Tetramethylstannane with sodium and liquid ammonia gives $(CH_3)_3SnNa$, $NaNH_2$ and CH_4; tetraphenylstannane behaves similarly but some of the sodium triphenylstannide is further substituted yielding the disodium salt.[1] Bis(trimethylstannyl)-methane and bis(trimethylstannyl)ethylene react with sodium in liquid ammonia, the former according to the following equations: $CH_2[Sn(CH_3)_3]_2 + 2Na + NH_3 \rightarrow (CH_3)_3SnNa + (CH_3)_3SnCH_3 + NaNH_2$; $(CH_3)_3SnCH_3 + 2Na + NH_3 \rightarrow (CH_3)_3SnNa + CH_4 + NaNH_2$ and the latter according to the equations: $(CH_3)_3SnCH = CHSn(CH_3)_3 + 2Na + NH_3 \rightarrow (CH_3)_3SnNa + CH_2 = CHSn(CH_3)_3 + NaNH_2$; $CH_2 = CHSn(CH_3)_3 + 2Na + NH_3 \rightarrow CH_2 = CHSn(CH_3)_2Na + CH_4 + NaNH_2$.[1]

Triethyl-, tripropyl-, tributyl- and triamyl-silicyl fluorides do not react with sodium in liquid ammonia at its boiling point.[1] Sodium does not react with triethylgermanyl bromide in liquid ammonia but only with the ammonium bromide formed by ammonolysis: $2(C_2H_5)_3GeBr + 3NH_3 \rightarrow [(C_2H_5)_3Ge]_2NH + 2NH_4Br$; $2NH_4Br + 2Na \rightarrow 2NaBr + 2NH_3 + H_2$.[1]

Sodium triphenyl stannide is formed when triphenylstannyl bromide and iodide are treated with sodium in liquid ammonia. Trimethylstannyl bromide is reduced to sodium trimethylstannide. An almost quantitative yield of hexamethylstannoethane is obtained if only one equivalent of sodium is used: $2(CH_3)_3SnBr + 2Na \rightarrow (CH_3)_3Sn{-}Sn(CH_3)_3 + 2NaBr$. Dimethylstannyl bromide is converted to the sodium salt.

The heats of reaction of trimethylstannyl bromide with sodium in liquid ammonia are as follows: $(CH_3)_3SnBr,NH_3am + Na \rightarrow (CH_3)_3Sn + NaBr\ am$ - 30,470g.-cal.; $(CH_3)_3SnBrNH_3am + 2Na \rightarrow (CH_3)_3SnNa + NaBr\ am$ - 34,300 g.-cal.; $(CH_3)_3SnBr + Na \rightarrow NaBr + (CH_3)_3Sn$ - 37,470g.-cal.[1]

The free group, diphenyltin $(C_6H_5)_2Sn$, or the disodium salt $Na_2Sn(C_6H_5)_2$, is obtained by the action of sodium in liquid ammonia on diphenyltin dibromide or diiodide, depending upon the amount of sodium used. Dimethyltin dibromide is converted to the compounds, $(CH_3)_2Sn$, $(CH_3)_2SnNa_2$ or $NaSn(CH_3)_2Sn(CH_3)_2Na$, again depending upon the amount of sodium used in liquid ammonia solution.[1]

Other reactions of organohalides of tin and lead with sodium in liquid ammonia are tabulated by Watt.[1]

Triphenylgermanium oxide reacts with sodium in liquid ammonia to form sodium triphenylgermanide and triphenylgermanolate: $[(C_6H_5)_3Ge]_2O + 2Na \rightarrow (C_6H_5)_3GeNa + (C_6H_5)_3GeONa$. Trimethylstannyl phenoxide $(CH_3)_3SnOC_6H_5$ is converted to sodium phenoxide and either trimethylstannyl or sodium trimethylstannide depending upon the quantity of sodium used. Trimethyl stannyl hydroxide reacts according to the equation: $(CH_3)_3SnOH + Na \rightarrow (CH_3)_3Sn + NaOH$. Trimethylstannylamine reacts with sodium in liquid ammonia as follows: $(CH_3)_3SnNH_2 + 2Na \rightarrow (CH_3)_3SnNa + NaNH_2$. Reactions of organometallic compounds of tin and lead with solutions of metals in liquid ammonia are tabulated by Watt and many references are given.[1]

Organo antimony compounds of the type $(C_6H_5)_2SbI$ react with sodium in liquid ammonia to form sodium salts, $(C_6H_5)_2SbNa$ and possibly $(C_6H_5)_2Sb$.[1] Organobismuth halides give highly reactive deep red coloured compounds of the type R_2BiNa in liquid ammonia solutions of sodium and although they decompose slowly they are sufficiently stable to react promptly with $R'X$ compounds (where X = halide) giving unsymmetrical organobismuth compounds, $R_2R'Bi$, and a water soluble type, $R_2BiC_6H_4COOH$.[44]

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REACTIONS OF SODIUM WITH ORGANIC COMPOUNDS

Sodium organo compounds may be divided roughly into three main groups: those in which the metal is bonded to the carbon atom as in sodium methyl, $NaCH_3$, and sodium phenyl, NaC_6H_5, those in which the 'activity' of the C–H link is increased by attachment of doubly linked or aromatic radicals as in sodium benzyl, $NaCH_2C_6H_5$, and sodium triphenylmethyl, $Na(C_6H_5)_3CH$, and, lastly, derivatives of hydrocarbons containing acidic hydrogen, such as derivatives of acetylene and the monosubstituted acetylenes.

The first group are colourless salt-like compounds, insoluble in paraffin hydrocarbons and benzene, very reactive towards other organic compounds, extremely sensitive to air and moisture, spontaneously inflammable in air, and non-conducting in the fused state or in solvents other than dimethyl zinc.

The second group are highly coloured, usually orange or red, soluble in organic solvents, sensitive to air and moisture, generally spontaneously inflammable in air and electrically conducting in solution.

Members of the third group are salts. They are colourless and insoluble and are hydrolyzed by ionizing solvents such as water and alcohol. They are readily oxidized but are usually stable in air at ordinary temperatures.[1]

The thermal decomposition of sodium methyl is represented by the equation: $8NaCH_3 \rightarrow 6CH_4 + Na_2C_2 + 6Na$. The main reaction in the spontaneous decomposition of sodium ethyl at ordinary temperatures is: $2NaC_2H_5 \rightarrow Na_2C_2H_4 + C_2H_6$; at 90°–100°C., the products are sodium hydride and ethylene: $NaC_2H_5 \rightarrow NaH + C_2H_4$. Some ethane is also formed.[2]

Compounds of the type RNa react rapidly at or near room temperature with diphenylethylene, ketones, acid chlorides, ammonia, water and aqueous hydrochloric acid. The order of increasing 'reactivity' of the alkali metal compounds measured by Gilman and Young by (*a*) the reaction between benzonitrile and phenylacetenyl alkali metal compounds, (*b*) the metallation of dibenzofuran and ethyl alkalimetal compounds and (*c*) the reactions of ketyls with *n*-butyl chloride, is RLi, RNa, RK, RRb, RCs. The reactivity is also influenced by the R group.[3]

Free hydrogen at room temperature decomposes the reactive organometallic compounds: $C_6H_5Na + H_2 \rightarrow C_6H_6 + NaH$; the speed of such reactions increases in the order, C_6H_5Li, C_6H_5Na, C_6H_5K, C_6H_5Rb, C_6H_5Cs.[4]

Organometallic compounds may be considered as salts derived from the weakly acidic RH compounds: $2RH + 2M \rightarrow 2RM + H_2$. The order of acidity is: $C_2H_6 < C_6H_6 < CH_3C_6H_5 < CH_2(C_6H_5)_2 < CH(C_6H_5)_3 <$ xanthen < aniline < fluorene < phenylacetylene < alcohols < phenol. Thus, sodium phenyl may be obtained from sodium ethyl, and sodium benzyl from sodium phenyl: $NaC_2H_5 + C_6H_6 \rightarrow NaC_6H_5 + C_2H_6$; $NaC_6H_5 + C_6H_5CH_3 \rightarrow NaCH_2C_6H_5 + C_6H_6$.[5] The stability of metal organo compounds has been studied by Jaffé and Doak[6] and the electrolytic nature of organo-alkali compounds by Ziegler *et al.*[7]

Sodium organo compounds are prepared by the action of sodium on mercury dialkyls or diaryls: $Hg(CH_3)_2 + 2Na \rightarrow 2NaCH_3 + Hg$. In order to exclude oxygen, moisture and carbon dioxide, these reactions were first carried out in sealed evacuated vessels but it has since been shown that the reactions may be carried out successfully in a stream of pure dry nitrogen. Schlenk and Holtz[8] have thus prepared sodium methyl, sodium ethyl, sodium propyl, sodium octyl, sodium phenyl and sodium benzyl. Sodium methyl is prepared in ligroin, b.p. about 80°C., sodium ethyl and propyl in a higher boiling ligroin, b.p. 100°–150°C., and sodium octyl, phenyl and benzyl in benzene. Sodium ethyl has been prepared by Gilman and Young by stirring 0·04g.-atoms of sodium in petroleum ether, b.p. 68°–77°C., with 0·01mole of mercury diethyl for one and a half days in a stream of pure dry nitrogen.[3] Sodium reacts with di-*sec.*-butylmercury in dodecane at 20°–25° in an atmosphere of nitrogen to give a reaction mixture which on subsequent treatment with carbon dioxide, followed by water, yields an aqueous layer from which the two acids, CH_3-$(C_2H_5)CHCOOH$ and $CH_3(C_2H_5)C(COOH)_2$ may be isolated. At room temperature 0·07mole of sodium and 0·016mole of di-*sec.*-butylmercury stirred for eight days in an apparatus swept out with nitrogen yield gases which on passage over bromine give 0·013mole of butene as dibromobutane and 0·004–0·005moles of butane. No 3:4-dimethylhexane has been isolated from the residue.[9]

Sodium alkyls and aryls are also formed by the action of sodium in benzene on the corresponding organo halides.[10] Chlorides are more effective than bromides and bromides than iodides in the formation of alkali metal organo compounds.[11,12]

High surface sodium, adsorbed on inert solids and suspended in a non-reactive liquid, is used for the preparation of sodium alkyls and aryls. For example, sodium amyl is obtained by adding amyl chloride to high surface sodium adsorbed on zircon and suspended in petroleum ether at 0° to 10°C. Subsequent carbonation with solid carbon dioxide, followed by acidification with a mineral acid yields caproic acid which is extracted with ether or benzene.[13] Sodium amyl is also prepared using dispersed sodium. To prepare sodium dispersions clean, dry apparatus must be used; the sodium is melted in an inert medium which boils at a temperature above that of the m.p. of sodium; heptane, *n*-octane, toluene, xylene, naphtha, kerosene, mineral oil and *n*-butyl ether are suggested solvents. A small amount of dispersing agent such as aluminium laurate, octoate or stearate, calcium stearate, copper oleate, zinc stearate, cellulose nitrate or butadiene, 0·01 to 2% of the total weight of reactants, is added to the mixture which is vigorously agitated mechanically at 100°–110°C. The most efficient agitator is one which revolves at a high speed in the fluid mixture so that both sodium and the inert medium are drawn up into a cylinder and discharged through slots. The high tangential shear produced at the exterior surface of the cylinder as the mixture issues from the slots causes the reduction of the particle size of the sodium to the range of submicron to 20 microns in diameter. The use of a baffled vessel reduces swirl. The advantages of sodium dispersions in carrying out organic reactions are many. The particles react completely before a protective film is formed; reactions may often be completed in minutes instead of hours; violent surging of reactions may be avoided by adding the dispersion at a controlled rate; an increased yield is usually obtained, a lower reaction temperature is required and side-reactions are decreased. Reactions may be carried out over a wide range of temperature, -80°C. to 400°C., and more expensive reagents such as sodium alcoholates, sodium hydride, sodamide, triphenylmethyl sodium can in many cases be replaced by sodium in this form.[14]

Sodium and amyl chloride in *iso*propylbenzene at $-6°$ to $-11°$C. on standing overnight yield, when subsequently carbonated and acidified, cumic acid with a smaller amount of the *o*-acid.[15]

Sodium amyl, prepared from sodium and amyl chloride at $-10°$C. by stirring at 5,000r.p.m. with *n*-heptane as solvent, when stirred at 10,000r.p.m. for a further 1·5hr., yields on carbonation with solid carbon dioxide about 85% of the sodium salt of caproic acid and some 3–7% of decane. Similar runs at 50°C. for 3hr. yield also about 4% of a water-soluble pentenedicarboxylic acid. When one equivalent of sodium *tert.*-amylalcoholate is added to the mixture before stirring and the mixture is heated at 50°C. for 3hr., subsequent carbonation yields 33% of sodium caproate, 11% of decane, 34% of the water-soluble pentenedicarboxylic acid and metallic sodium.[16]

Sodium amyl, sodium and anisole react, preferably in the presence of certain alkoxides, forming the amyl derivative, *o*-$C_5H_{11}C_6H_4OCH_3$. *o*-Cresol methyl ether may be alkylated similarly.[17]

When heated with sodium amyl and an alkoxide, benzene is dimetallated chiefly in the *meta* positions but the ratio of *meta* to *para* can be altered by the choice of alkoxide associated with the reagent. Thiophen is readily dimetallated in the 2:5 positions, *p-tert.*-butylphenol in the 2:6 positions and *iso*propylbenzene and *sec.*-butylbenzene in the 3:5 positions.[18]

Sodium and sodium amyl are used for the metallation and cleavage of ethers, principally alkylphenyl ethers; thus methyl phenyl ether yields the sodium derivatives, *o*-$NaC_6H_4OCH_3$, $NaOC_6H_5$ or *o*-$C_5H_{11}C_6H_4OCH_3$ according to the temperature at which the reaction is carried out. Other alkylphenyl ethers undergo metallation and cleavage in a similar manner but metallation is not always a prerequisite to cleavage. Methyl phenyl ether is attacked by sodium alone to give the sodium derivatives *o*-$NaC_6H_4OCH_3$ and $NaOC_6H_5$.[19]

Sodium and amyl chloride at 20°C. react to form decane and some disproportionation products. In the presence of toluene the decane is largely replaced by hexylbenzene. The intermediate sodium compounds, sodium amyl and sodium benzyl, are insoluble in the medium. The yield of hexylbenzene is increased by the addition of certain salts and alkoxides.[20]

Sodium amyl and *iso*butene in pentane react, yielding on carbonation and acidification β-methylvinylacetic acid and β-methylglutaric acid; propene under similar conditions yields vinylacetic acid. Other similar reactions have been described.[21]

*iso*Butyl bromide and sodium react together to give sodium *iso*butyl which on carbonation yields the sodium salt of *iso*valeric acid: $(CH_3)_2CHCH_2Br + 2Na \rightarrow (CH_3)_2CHCH_2Na + NaBr$; $(CH_3)_2CHCH_2Na + CO_2 \rightarrow (CH_3)_2CHCH_2$-$COONa$.[22]

Triphenylchloromethane reacts with sodium in ether and benzene to give a 96% yield of sodium triphenyl.[23] When sodium is allowed to stand with triphenylchloromethane in benzene or ether in the presence of benzophenone, the metal first combines with the ketone to form the metal ketyl which reacts with the halogen compound yielding triphenylmethyl, sodium chloride and benzophenone. A similar reaction occurs when the ketone is replaced by tetraphenylethylene. Monochloro- and monobromo-benzene and butyl chloride are also carriers of sodium. A sodium halyl complex is first formed: $C_6H_5Br + Na \rightarrow C_6H_5\text{--}Br\text{--}Na\text{--}$ which may then react with triphenylchloromethane: $(C_6H_5)_3CCl + C_6H_5\text{--}Br\text{--}Na\text{--} \rightarrow (C_6H_5)_3C + NaCl + C_6H_5Br$, or react with another complex of the same kind: $2C_6H_5\text{--}Br\text{--}Na\text{--} \rightarrow (C_6H_5)_2 + 2NaBr$ or react with an atom of sodium: $C_6H_5\text{--}Br\text{--}Na\text{--} + Na \rightarrow C_6H_5Na + NaBr$. If left to itself the metal halyl eventually forms the free radical, phenyl and sodium bromide: $C_6H_5\text{--}Br\text{--}Na \rightarrow C_6H_5 + NaBr$.[24]

High surface sodium adsorbed on an inert solid suspended in benzene reacts with monochlorobenzene at 20°–30°C. to form sodium phenyl. Subsequent carbonation and acidification with mineral acid yields benzoic acid.[13] Sodium phenyl is also prepared when suitable sodium dispersions are treated with monochlorobenzene.[14]

Benzyl chloride when treated with dispersed sodium reacts to form 87–90% of dibenzyl: $2C_6H_5CH_2Cl + 2Na \rightarrow C_6H_5CH_2CH_2C_6H_5 + 2NaCl$.[14]

Propyl chloride and sodium in xylene yield propane, propylene and hexane.[25]

Organo chlorides and sodium in benzene treated with carbon dioxide at 30 lb. pressure give the following yields of acids from the corresponding chlorides: 76% of $p\text{-}CH_3C_6H_4COOH$, 58% of $m\text{-}CH_3C_6H_4COOH$, 12% of $p\text{-}C_6H_5C_6H_4COOH$, 28% of $p\text{-}(CH_3)_2NC_6H_4COOH$, 45% of C_6H_5COOH. Tertiary carbinols are formed when the reaction is carried out in the presence of diethyl carbonate. For example, 0·1mole of the chloride, $C_6H_5C_6H_4Cl$, 0·42mole of diethyl carbonate and 0·22g. of sodium wire in 100ml. of benzene heated for 10hr. yield 23% of the pure tertiary carbinol, $(C_6H_5C_6H_4)_3COH$. Monochlorobenzene gives 66% of the carbinol $(C_6H_5)_3COH$. Numerous other similar condensations have been described. Caution is necessary in carrying out these reactions; if the reaction becomes uncontrolled it proceeds with explosive violence. Methods of removing the protective film which forms on the sodium surface are discussed.[26]

Sodium acts on 1:4-dibromo-2-butene in dry ether at room temperature to give 1:8-dibromo-2:6-octadiene which is then transformed into 1:6-octadiene, dodecatriene and unsaturated higher analogues. No products of composition other than a multiple of four carbon atoms are isolated nor are any cyclic products formed.[27]

A yellowish halogen-free polymer, $(C_6H_4)_4$, is obtained when a mixture of 2:3-dibromo-1:3-*cyclo*hexadiene and sodium in dry dioxan is kept for two days in a sealed tube.[28]

The reaction of 1:4-dibromo-2-*cyclo*hexene with sodium in boiling xylene yields 1:3-*cyclo*hexadiene. If the solvent is not heated, the product, 1:2-dibromo-3-*cyclo*hexene is formed.[29]

The compounds, dimethylvinylcarbinol, $CH_2{=}CHC(OH)(CH_3)_2$, acetylene and ethylene are obtained when vinyl bromide and acetone in ether are added dropwise for 10hr. to sodium sand in ether with cooling.

When the mixture formed by adding vinyl bromide and acetone in ether dropwise for 10hr. to sodium sand in ether with cooling is decomposed with ammonium chloride, extracted with ether and distilled, the products, 2-methyl-3-butene-2-ol, $CH_2{=}CHC(OH)(CH_3)_2$, acetylene and ethylene are obtained. Small amounts of mesityl oxide and pinacol and butadiene are also formed.[30]

A series of alcohols has been prepared by the reaction of organic chlorides with carbonyl compounds in the presence of finely divided sodium. Alcohols so prepared are: 2-benzyl-2-propanol, $(C_6H_5CH_2)_2CH(OH)CH_3$, $[(CH_3)_2CH]_2\text{-}C(OH)CH_2C_6H_5$, 2:6-dimethyl-4-benzyl-4-heptanol, $C_6H_5CHCH(OH)C_2H_5$, $[(CH_3)_2CH]_2C(OH)C_6H_5$, $C_6H_5CH(OH)C_2H_5$, 6-methyl-6-undecanol, 2-methyl-4-

*iso*butyl-4-nonanol and 2:4-dimethyl-3-*iso*propyl-3-pentanol.[31]

When a mixture of carbon tetrachloride and sodium is subjected to shock by striking with a hammer the reaction is violently explosive; with chloroform a moderately strong reaction occurs. The alkali metals act as powerful detonators with organic halogen compounds and the order of the power of the explosion decreases from sodium-potassium alloy through potassium, sodium to lithium.[32,33]

On slightly warming a mixture of carbon tetrachloride with a 1% sodium amalgam, a brisk reaction occurs: $4Na + CCl_4 \rightarrow 4NaCl + C$.[34]

A summary of the work carried out by Polanyi and his collaborators up to 1942 on the atomic reactions of sodium with organic halides by the sodium 'flame' method has been given by Bawn,[35] who describes experimental procedures and theoretical considerations, with numerous references to the literature. A later review by Warhurst[36] is mainly concerned with developments up to 1951.

By measuring the reaction velocity of alkyl halides with sodium vapour by the diffusion flame method it has been shown that the reaction inertia decreases in the order; F, Cl, Br, I for the halides of a given radical; with increase in length of the carbon chain; with increase in the number of chlorine atoms and the more so the closer these are together, and with the introduction of carbonyl oxygen. The inertia also decreases in the order: primary, secondary, tertiary halides but is not affected by branching of the chain. The reaction is retarded by a double linking at the carbon atom to which the chloride is attached, but the inertia is reduced if the double linking occurs at the next carbon atom. A small reaction inertia appears to be associated with a large dipole moment.[37]

A few examples of reactions of sodium vapour in a highly diluted state with organic halides are given below.

A rapid gas reaction occurs and free radicals are formed when nitrogen at a few mm. pressure is passed with sodium vapour at 10^{-3}mm. and at about 270°C. into a space filled with an alkyl halide. The presence of free radicals is substantiated by the induced chlorination of methane. A sodium-loaded methane stream is passed into methyl bromide and at a point where all the sodium is used up, the gas stream containing the free radicals and methane is allowed to react with chlorine: $Na + CH_4 + CH_3Br \rightarrow NaBr + CH_3 + CH_4$; $CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$; $Cl + CH_4 \rightarrow CH_3 + HCl$. The resulting chlorination of methane is 0·1 to 0·5 the intensity of that by direct use of sodium, methane and chlorine: $Na + Cl_2 \rightarrow NaCl + Cl$; $Cl + CH_4 \rightarrow CH_3 + HCl$; $CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$. By substituting iodine for chlorine and using methyl bromide or ethyl bromide, and cooling the products in cold traps, methyl iodide or ethyl iodide may be isolated in yields of 10% for a sodium pressure of 5×10^{-4}mm. and 2% for a pressure of 10^{-2}mm. The yield increases with increase in rate of flow.[38] The free radicals react with hydrogen at 300°–500°C. to give methane: $CH_3 + H_2 \rightarrow CH_4 + H$. In the absence of hydrogen the free radicals are dimerized: $2CH_3 \rightarrow C_2H_6$.[39]

Whereas the principal product in the reaction of sodium vapour with methyl iodide is ethane, some methane, ethylene and hydrogen are also formed. With ethyl iodide the main product is butane with smaller amounts of ethane, ethylene, methane and hydrogen. Some propane is also present and is considered to be a pyrolysis product of butane. It is concluded that at low temperatures the dominant reaction for both methyl and ethyl radicals is a combination of the two to form a saturated hydrocarbon. At higher temperatures disproportionation and reaction with other molecules occur.[40]

Sodium vapour in a highly diluted state reacts with monochlorobenzene to give a 90% yield of diphenyl. Dibenzyl is obtained from benzyl chloride.

The cyanogen radical is formed from cyanogen chloride or cyanogen.[41] The vinyl radical, set free when sodium vapour reacts with vinyl chloride or bromide, reacts with hydrogen to form ethylene. Disproportionation of the vinyl radical leads to the formation of acetylene and ethylene.[42]

Little or no luminescence is observed when monohalogen organic compounds react with sodium in the highly diluted state, but an intense luminescence of the *D*-line of sodium is produced when the number of halogen atoms is increased. All the saturated dihalides so far examined show this characteristic luminescence. $RX_2 + Na \rightarrow NaX + -RX$; $-RX + Na \rightarrow NaX + R$. The excitation reaction is the exothermal rearrangement of the reaction product R, whereby an unsaturated molecule may be formed either by the closure of a double bond or migration of a hydrogen atom: $CH_2BrCH_2 + Na \rightarrow NaBr + CH_2 = CH_2$; $-CH_3CHBr + Na \rightarrow NaBr + CH_2 = CH_2$; or a cyclic molecule may be produced; $-CH_2BrCH_2CH_2 + Na \quad NaBr + \underbrace{CH_2-CH_2-CH_2}$. The internal energy carried by the sodium halide is transferred to a sodium atom by collision, thus producing luminescence.[35]

The primary reaction of sodium vapour with trifluoromethyl iodide, bromide and chloride is shown by the diffusion flame method to be: $CF_3I + Na \rightarrow NaI + CF_3$. The activation energies for the iodide, bromide and chloride are 1·7, 2·3 and 7·0kg.-cal. per mole respectively. The free CF_3 radicals combine to give hexafluoroethane, C_2F_6, but if hydrogen is used as the carrier gas trifluoromethane is formed: $CF_3 + H_2 \rightarrow CHF_3 + H$. The simultaneous formation of tetrafluoroethylene is due to the decomposition of CF_3 radicals. Carbon tetrafluoride does not react with sodium under the conditions of the sodium flame reaction.[43] The kinetics of the diffusion flame reaction between sodium vapour and some fluorinated methyl halides are described by Reed.[44]

The theory of diffusion flames is discussed by Cvetanovic and Le Roy with particular reference to the reaction of sodium atoms with ethyl chloride.[45]

The steric factor and activation energy of the reaction: $Na + C_2H_5Cl \rightarrow NaCl + C_2H_5$ has been studied over the range of 260°–380°C. by the diffusion flame method. The activation energy is 10·2kg.-cal. per mole ± 0·5kg.-cal. The steric factor is 1·0 ± 0·3 based on the customary value assigned to the collision diameter.[46] The inductive effect and chemical reactivity with respect to reactions of halides with sodium atoms has been studied by Smith and Eyring. Attempts are made to explain differences in activation energy for similar reactions of a homologous series by calculations of charge distribution.[47,48]

Meer and Polanyi have made a comparison of sodium vapour reactions with other chemical reactions.[49]

Hartel and Polanyi[39] give the following values for the heats of activation in reactions of halogen alkyls with atomic sodium: $Na + RX = NaX + R$ where R is the alkyl and X the halide radical. The values expressed as kg.-cal. are: $CH_3F > 25$; CH_3Cl, 8·8; CH_3Br, 3·2; CH_3I, 0; CH_2Cl_2, 5·0; $CHCl_3$, 2·0; CCl_4, 0; C_2H_5Cl, 7·3; C_2H_5Br, 4·4; C_2H_5I, 1·7. Activation energies expressed as kg.-cal. for reactions of organic halides with sodium atoms have been given by Gieb:[50] CH_3I, C_6H_5I, $C_6H_5CH_2Cl$, C_6H_5COCl, CH_3COCH_2Cl, 0; CCl_4, 1; C_2H_5I, 1·7; CH_3COBr, CH_3COCl, CNCl, 2·0; *n*-C_3H_7I, CH_3Br, C_6H_5Br, $CHCl_3$, 3·0; C_2H_5Br, $CH_2 = CHCH_2Cl$, $CH_3CH_2CHCl_2$, 4; $C_2H_5(CH_3)_2CCl$, CH_3CHCl_2, 5; $(CH_2Cl)_2$, CH_2Cl_2, 5·2; $(CH_3)_3CCl$, $C_2H_5CH_2CHCl$, 5·5; $CHCl = CHCl$ *cis* and *trans*, *n*-$C_5H_{11}Cl$, $C_5H_{11}Cl$(l *iso*) 6; $(CH_3)_2CHCl$, *n*-C_4H_9Cl, *iso*-C_4H_9Cl, 6·5; $CH_2 = CClCH_3$, *n*-C_3H_7Cl, 7; C_2H_5Cl, C_6H_5Cl, 7·5; $CH_2 = CHCl$, CH_3Cl, 9; $CH_3 > 25$.

The experimental results of Hartel, Meer and Polanyi[37] for the rates of reaction in the gaseous phase of $RCl + Na \rightarrow NaCl + R$ where R is CH_3, C_2H_5, *n*-C_3H_7, *iso*-C_3H_7, *tert.*-C_4H_9 have been shown by Taft[51] to fit the equation:

log K/K_0 (or K/K_0) = $\sigma^*\rho^*$ where σ^* is a polar substituent constant for the group R relative to the standard methyl group and ρ^* is a constant giving the susceptibility of a given reaction series to polar substituents. A value of $\rho^* = 2{\cdot}480 \pm 0{\cdot}174$, probable error 0·05, is given for the vapour phase reactions of alkyl chlorides with sodium.

When vinyl iodide is allowed to react with sodium vapour in the 'diffusion flame', the predominant gaseous products are ethylene, acetylene and butadiene. It is considered likely that these compounds are formed by disproportionation and recombination of vinyl radicals. In the presence of hydrogen, ethylene is also formed: $C_2H_3 + H_2 \rightarrow C_2H_4 + H$. More vinyl iodide than sodium is used up in the reaction and a non-volatile organic iodide is formed; this has an important bearing on the calculation of the rate constant of the primary process.[52]

The action of organo metallic compounds on optically active halides tends to produce racemization as the carbon-halogen bond ionizes and the carbon-metal bond resists ionization. Lane and Ulrich[53] have carried out the Wurtz synthesis with optically active halides; their results support Morton's mechanism[54] rather than that involving free radicals.

Addition of sodium to double linkages may take place by a simple 1:2-addition: $(C_6H_5)_2C{=}C(C_6H_5)_2 + 2Na \rightarrow (C_6H_5)_2CNa.CNa(C_6H_5)_2$ or by a dimerizing addition: $(C_6H_5)_2C{=}CH_2 + 2Na + H_2C{=}C(C_6H_5)_2 \rightarrow (C_6H_5)_2CNaCH_2CH_2CNa(C_6H_5)_2$. Although tetraphenylethylene adds sodium, it does not add bromine, lithium or potassium. Sodium-potassium alloy, however, gives the dipotassium addition product probably through the intermediate formation of the sodium compound.[55]

The styrenes, $C_6H_5CH{=}C(CH_3)_2$, $C_6H_5CCH_3{=}C(CH_3)_2$, $(C_6H_5)_2C{=}CHCH_3$, $(C_6H_5)_2C{=}C(CH_3)_2$,[56] do not add sodium. Sodium does not combine with the following compounds: $(p\text{-}CH_3C_6H_4)_2C{=}C(CH_3)_2$, $(C_6H_5)_2C{=}CHC_2H_5$, $(C_6H_5)_2C{=}CHC_3H_7$ or $(C_6H_5)_2C{=}CHC_4H_9$.[57]

Reaction of sodium in ether with α-methylstilbene is rapid and a dark brown addition product is formed which reacts with alcohol to give α-methyldibenzyl. Anisal fluorene and sodium give a bright orange-red addition product which is decomposed by alcohol to 1:4-diphenylene-2:3-dianisylbutane. Sodium, fluorene and α-naphthaldehyde give α-naphthylidene fluorene and some 1-biphenylene-4-naphthyl-1:3-butadiene which is coloured deep yellow. The fluorene compound with sodium in ether gives an indigo-blue product decomposed by alcohol to 9-α-naphthomethylfluorene.[57]

Olefines such as styrene, 1-phenylbutadiene, butadiene and isoprene are polymerized by sodium powder, the last two compounds giving sodium rubbers. A small amount of sodium can convert many olefine molecules to large molecules or polymers: $RCH = CH_2 + R^1Na \rightarrow RCHNaCH_2R^1$; $RCH = CH_2 + RCHNaCH_2R^1 \rightarrow RCHNaCH_2CHRCH_2R^1$ and so on.[58]

The addition of 0·01 to 0·5 parts of 1:2-butadiene per 100 parts of monomeric material improves the pressing characteristics of synthetic rubbers obtained by the catalytic polymerization of monomers with finely divided sodium.[59] In the polymerization of butadiene with sodium catalyst, addition of a small amount of a hydroxy ether produces a product resembling natural rubber in processing characteristics.[60-63]

The action of sodium on piperylene, triphenylmethane and fluorene has been described.[64]

The mechanism of the addition of sodium to double linkings has been discussed by Schlenk and Bergmann[65] and the kinetics of polycondensations of compounds, such as 1:3-butadiene, $CH_2 = CHCH = CH_2$, with sodium studied by Bauer and Magat.[66]

A variety of uses for metallic sodium in the plastic industry for the manufacture of monomers, polymers, plasticizers and stabilizers are described by Sittig.[67]

Whereas the alkali metals alone do not catalyze the polymerization of ethylene, propylene or their mixtures, the catalytic effect of the oxides of chromium, molybdenum, tungsten or uranium is promoted by the addition of the alkali metals. In the examples given, sodium is used as the promoter.[68]

The polymerization of bivinyl by means of thin layers of sodium is complete in two hours at room temperature when the sodium layer is formed by condensation at -180°C., after 25hr. when the sodium layer is formed at -68°C., and after 48hr. at a sodium condensation temperature at 0°C. The crystallization effects of sodium at these temperatures accounts for the activity changes.[69]

Acetylides are formed by the action of acetylene on heated sodium or on a solution of the metal in liquid ammonia (see page 522).

Monoalkylacetylenes and sodium form similar metal derivatives such as $CH_3C \equiv CNa$.[3]

Phenylacetylene and sodium stirred in ether under pure dry nitrogen react at room temperature and on carbonation give a 74% yield of phenylpropiolic acid.[3]

Fluorene and high surface sodium, adsorbed on an inert solid suspended in an inert medium, yield sodium fluorenyl.[13]

Dibenzofuran reacts with sodium ethyl to give a disodium derivative, whereas lithium ethyl yields only a monolithium derivative.[55]

Alkali metals add to naphthacene or 1:2:3:4-tetrahydronaphthacene in nitrogen in the presence of ether or glycol dimethyl ether, yielding heteropolar complexes which contain ethers.[70,71]

Sodium reacts with a solution of naphthalene in 1:2-dimethoxymethane to produce a dark green solution which contains a compound of empirical formula $C_{10}H_8Na_2$. The solution reduces iron, nickel or cobalt chlorides to a finely divided metallic powder.[72]

Mixed catalysts, composed of sodium and a nitrogen-containing heterocyclic compound, are used for the condensation of aromatic compounds with unsaturated compounds. The products are useful intermediates in the preparation of detergents, insecticides, dyes and medicinals.[73]

Monosodium buccocamphor heated at 240°C. yields 2:3-dihydroxycymene, tetrahydrocarvone, carvacrol and polyhydroxy compounds. No hydrogen is evolved.[74]

The iron catalyst used in the Fischer-Tropsch reaction for the synthesis of liquid fuels from carbon monoxide and hydrogen is improved by the presence of a small amount of less than 10% alkali metal promoter and about 2–10% of finely divided carbon particles.[75]

By treating lard at 55°–170°C. for 3–120min. in the presence of 0·15–1·0% of alkali metal catalyst, it is converted to a beta crystalline modification as opposed to the normal beta form for processed lard. In this way its appearance, keeping and baking properties are improved.[76]

Sodium reacts with alcohols to form alcoholates and hydrogen: $Na + CH_3OH \rightarrow NaOCH_3 + 0{\cdot}5H_2$. The greater the number of carbon atoms in the molecule, the less rapid is the reaction; the rate of reaction also decreases from primary to secondary to tertiary alcohols.

The rates of reaction of sodium with ethyl alcohol and ethyl alcohol-water mixtures have been studied by Schnurmann. The view has been expressed that when a metal dissolves in a medium in which a gas is evolved, the size of the gas bubble influences the access of the reactive component of the liquid to the metal surface, and the larger are the adhering gas bubbles the smaller is the rate of dissolution of the metal. The size of the bubble is controlled by the viscosity of the reacting liquid. The results obtained by Schnurmann show that the higher the viscosity of the medium the more rapid is the reaction. In Table LI the weight of sodium is approximately the same in each case but the viscosity of the medium is altered by adding water; in Table LII the weight of sodium has been varied; the addition of larger pieces of sodium causes a greater increase in viscosity than the addition of smaller ones.

TABLE LI. - RATE OF REACTION OF SODIUM IN ETHYL ALCOHOL-WATER MIXTURES

% C_2H_5OH in water	Time of dissolution sec.
Once distilled over CaO	123
95	85
91	57
86·4	38
82·6	45
67	45
60	32

TABLE LII. - RATE OF REACTION OF SODIUM IN ABSOLUTE ETHYL ALCOHOL

Wt. of Na mg.	Time of dissolution, *T* sec.	Specific time of dissolution, *t*
198	607	3·1
120	425	3·5
109	397	3·6
95	365	3·8
80	360	4·5
65	271	4·2

($t = T/$wt. of Na)

Sodium is found to dissolve more rapidly in alcohol at a lower temperature than at a higher one; the addition of urea also causes a more rapid reaction.[77] No reaction occurs when sodium is treated with alcohol below −48°C.

The velocity of solution of sodium in solutions of ethyl alcohol or methyl alcohol in benzene, toluene or xylene is not constant over the solution reaction but drops as the concentration of alcohol falls. The rate of solution is proportional to the concentration of the hydrogen ions. The temperature coefficient of the reactions and the accelerating effect of stirring indicate the diffusive nature of the process.[78,79]

Measurements have been reported for the current produced when sodium is dissolved in methyl or ethyl alcohol, for the electrolytic decomposition of the alkoxides, the ionic mobilities and the degree of dissociation of the compounds. All the values are similar to those for sodium ions in aqueous solution. Alcoholates appear to resemble metallic hydroxides rather than true organic compounds.[80]

The solvation of sodium ions in methyl and ethyl alcohols and in acetone and acetophenone, based on the apparent molecular volume, has been calculated from published data.[81]

An incident has been described in which sodium covered with sodium methoxide or butoxide, formed in the presence of toluene, exploded when thrown into water.[82]

The production of sodium methoxide on an industrial scale by reaction of sodium with excess of alcohol has been patented. Excess alcohol, including alcohol of crystallization, is distilled off in the presence of an organic solvent such as an aliphatic or aromatic hydrocarbon which is inert to the alkoxide.[83]

The use of sodium amalgam as a raw material in the industrial preparation of sodium methoxide has been discussed from the technical and economic viewpoint by Nicolai.[84]

Alkaline earth metals are separated from alkali metals by treatment with lower aliphatic alcohols which do not affect the alkaline earth metal.[85] Calcium is recovered from mixtures containing sodium by vigorous agitation in an inert hydrocarbon, to liberate the calcium and disperse the sodium as small particles throughout the medium at a temperature above the melting point of sodium. The resulting mixture is separated into fractions, one containing essentially sodium dispersed in the inert medium and the other containing most of the calcium. The latter fraction is treated with an excess of one of the lower aliphatic alcohols when the undissolved calcium separates from the reaction mixture.[86]

Ethyl alcohol is oxidized when sodium amalgam is agitated with oxygen at room temperature in the presence of alcohol; acetaldehyde is formed, partly in the resinified form because of the action of the alkali. It is also formed when the oxygen is under pressure.[87]

Sodium and absolute alcohol reduce ethyl benzoate mainly to hexahydrobenzoic acid, but a small amount of tetrahydrobenzyl alcohol is also formed. Benzyl alcohol is reduced to toluene, benzaldehyde to toluene and benzoic acid. Nitrobenzene is converted principally to aniline but a small amount of hydrazobenzene, $(C_6H_5NH)_2$, is also formed. Phenol, phenyl ethyl ether and aniline are not appreciably attacked.[88]

Sodium and absolute alcohol convert the hydrazone, oxime or semicarbazone of steroids with a 17-keto group to compounds with a semicyclic 17-double bond.[89]

Sodium and ROH compounds reduce β-substituted propionitriles to 3-alkoxypropylamines. The reaction is carried out with sodium sand in dry toluene.[90]

Sodium and industrial *iso*amyl alcohol containing 20% of the isomer of b.p. 128°C. and 80% of the isomer, b.p. 132°C., reduce glycerides to fatty alcohols. An azeotrope of 8% water and 92% alcohol is distilled off before adding the sodium.[91]

Sodium and butyl alcohol in xylene reduce vegetable oils such as Babassu oil and Ucuhuba fat to aliphatic alcohols.[92]

*cyclo*Hexanone with *iso*amyl nitrite in the presence of sodium gives a red nitroso compound; the *iso*amyl alcohol liberated reacts with sodium and the nitroso compound is reduced to 2-hydroxy*cyclo*hexanone oxime.[93]

The use of sodium in the preparation of 6-(*N*-methyl-*p*-tolylsulphonamido)-quinoline has been described.[94]

The synthesis of 2-ethylhexanol by condensation of butanol with sodium, using aluminium, zinc, copper, magnesium, etc., as co-catalysts, at 250°-310°C. in an autoclave is described by Kobayashi *et al.* The products of reaction are 2-ethylhexanol, butyric acid, a C_{12} alcohol, a C_8 fatty acid and esters. Aluminium is the most favourable co-catalyst to improve the yield of 2-ethylhexanol, while copper appears to accelerate the formation of higher molecular weight products.[95]

The metallation of sodium phenoxide has been studied by Morton and Letsinger;[96] carbonation affords *o*-hydroxybenzoic acid, 2-hydroxy*iso*phthalic acid and hydroxyterephthalic acid.

The reduction of acids by sodium at high pressures to form fatty alcohols for use in the detergent industry has been described by Kulkarni.[97]

Terephthalic acid is reduced by pure sodium amalgam in the cold to the Δ^2-tetrahydro acid which is easily further reduced to the hexahydro acid. With ordinary sodium amalgam only the $\Delta^{2,5}$-dihydro acid is formed. This acid is not further reduced until it has been rearranged into the $\Delta^{1,5}$- and $\Delta^{1,4}$-acids. This behaviour of sodium amalgam according to Willstätter *et al.* indicates that the reduction of an organic compound consists in the addition of sodium at the position of partial affinity of the molecule, and the replacement of the sodium atoms by hydrogen under the influence of water. According to the above authors, pure sodium amalgam does not evolve hydrogen on treatment with water. Impurities in the sodium amalgam catalytically accelerate the decomposition of sodium amalgam by water with liberation of hydrogen which competes with the addition of sodium atoms to the unsaturated groupings. The influence of the pH on the course of the reduction with sodium amalgam has been studied. The effect of the addition of 0·001 part of various metals to sodium amalgam is to accelerate the decomposition of water: copper and silver relatively little, magnesium and zinc more, aluminium still more, tin and especially lead most. Comparative experiments show that sodium amalgam prepared in iron crucibles decomposes water 30–50 times faster than electrolytic amalgam.[98]

When the unsaturated acid $C_6H_5CH{=}C(COOH)CH{=}CH_2$ is reduced in carbon dioxide with sodium amalgam, the compound $C_6H_5CH_2C(COOH){=}CHCH_3$ is obtained.[99]

Sodium dispersions are used to induce complete and rapid reaction of sodium with ethyl acetate; practically quantitative yields of acetoacetic ester, based on sodium, are obtained.[14,100] Sodium acetoacetic ester has also been prepared by the action of high surface sodium, adsorbed on an inert solid suspended in an inert medium, on ethyl acetate.[13]

Sodium reacts with ethyl trifluoroacetate and ethyl trifluoroacetodifluoroacetate, $CF_3COCF_2COOC_2H_5$, the former giving ethyl $\gamma{:}\gamma{:}\gamma$-trifluoroacetoacetate, and the latter ethyl trifluoroacetodifluoroacetate.[101]

Sodium reacts with the fatty acid ester, $(C_6H_5CH_2)_2CHCOOC_2H_5$ to give a 78–83% yield of tetrabenzylacetoin, together with a trace of the diketone.[102]

The triacetate and tribenzoate of phloroacetophenone and the diacetates and dibenzoates of quinacetophenone, resopropiophenone and resobutyrophenone in the presence of sodium in dry toluene are subjected to molecular rearrangement. The acetates give chromone derivatives, the benzoates, flavone derivatives except in the case of the compound, 2:4-$(C_6H_5COO)_2C_6H_5$-COC_3H_7 which gives benzoic acid.[103]

Ethyl *o*-benzoylbenzoate on treatment with sodium yields a deep scarlet solution which on concentration gives 3-phenylphthalide, some neutral polymeric material and a large acid fraction. The reduction of trimethylacetic acid derivatives has also been described.[104]

The reduction and condensation of aliphatic esters with acetophenone and sodium in an anhydrous medium have been studied by Wiemann, Mamlok and Sobolewski.[105]

Sodium is used as a catalyst in the reaction between cyanuric esters of the type $\underline{N{=}C(OR)N{=}C(OR)N{=}C}(OR)$ (where R is a univalent radical of a primary ethylenically unsaturated monohydric alcohol containing 3 to 10 carbon atoms) and polyhydric alcohols containing primary and secondary -OH groups, such as in glycerol and ethylene glycol, to give resinous products which may be used as coating and moulding compositions.[106]

Acetone or mesityl oxide and sodium react at the metal surface and if the metal is introduced all at once in a finely divided form the high surface area promotes interaction of the molecules attached to the surface and as much as 40% of polymeric product is formed. If, however, the metal is added progressively, negligible quantities of polymer are produced.[107]

The reduction of saturated ketones with sodium yields a mixture of glycols and alcohols. The rate of reduction is decreased and the yield of alcohol increased, the greater is the amount of alkyl substitution on the carbon atom adjacent to the carbonyl. It is suggested that the reduction in these reactions involves a surface phenomenon and is therefore affected by steric variations.[108]

o-Acetoxyacetoarones undergo molecular rearrangement on treatment with sodium, forming *o*-hydroxyaroyl acetones.[109] The action of sodium on aliphatic ketones in an inert medium is discussed by Drweski and Wiemann.[110]

The mechanism of the reduction of aromatic ketones by sodium amalgam and alcohol has been studied by Bachmann. The reduction of ketones to hydrols proceeds through the intermediate formation of ketyl radicals.[111] Pinacols are reduced quantitatively to hydrols by sodium amalgam in anhydrous ether-benzene. This reaction also takes place through the intermediate formation of free ketyl radicals.[112]

The industrial preparation of hydroquinone by the reduction of quinone with sodium amalgam and water is discussed by Nicolai.[84]

The reactions between sodium and aliphatic, aromatic and mixed ethers have been studied by Durand. Diethyl ether reacts slowly forming sodium ethoxide and hydrogen; di-*iso*amyl ether reacts slowly in the cold and vigorously at the boiling point at which the metal is liquid; anisole, phenetole and veratrole react rapidly when hot until the reaction mass solidifies. Benzoyl ethyl ether behaves similarly.[113]

Sodium reacts with mercaptans to form mercaptides: $Na + RSH \rightarrow NaSR + 0{\cdot}5H_2$.[114]

The reaction between mononitriles and monoacetylenes to give substituted pyrimidines and pyridines is brought about by the presence of catalytic quantities of sodium.[115]

Aromatic nitro compounds in the form of an emulsion in an aqueous reagent are reduced by sodium amalgam; high concentrations of nitro compounds give azo and hydrazo compounds, whereas low concentrations favour amine formation.[116] The reduction of aromatic nitro compounds or azo derivatives with sodium amalgam may be carried out in the presence of an aqueous reagent which reacts with the amalgam, and a stable, water-miscible solvent for the organic compound which separates readily from the aqueous caustic alkali solution produced.[117] The technical and economic aspects of the industrial preparation of hydrazobenzene by reduction of nitrobenzene with sodium amalgam have been discussed by Nicolai.[84] A process for the reduction of nitrobenzene to hydrazobenzene by treatment in aqueous alcoholic solution with sodium amalgam in the presence of carbon is described by Hallie.[118]

Aniline added in theoretical amounts to high surface sodium deposited on activated carbon and heated at 180°C. yields sodium anilide which reacts with alkyl halides to give alkylanilines.[13]

Sodium forms an additive compound with pyridine to which the structure $Na \ldots NC_5H_5 \ldots C_5H_5N \ldots Na$ has been assigned.[119]

Two compounds, $(C_5H_5N)_2Na$ and $(C_5H_5N)Na$, are formed when pyridine is treated with dispersed sodium in the presence of certain oxygenated solvents such as 1:2-dimethoxyethane and tetrahydrofuran.[120]

Aliphatic N,N-dialkylamides are not affected by sodium in boiling benzene but N,N-dialkylbenzamides react readily.[104]

Whereas 1-alkyl-3-chloropiperidines are dehalogenated by sodium, acyclic β-chlorotertiary amines are not only dehalogenated but also decomposed to amines and olefines.[121]

The behaviour of certain indicators with sodium organo-compounds has been discussed. Sodium in pentane reacts with the compound $(CH_2{=}CHCH_2)_2O$ to form $CH_2{=}CHCH_2Na$.[122]

Cellulosic materials such as starches and dextrins on treatment with an alcoholic solution of an alkali metal at 80°–115°C. are converted to a 2-mono-alkali glucopyranose polymer which reacts with an alkyl halide to form an ether in which the organic group is attached to the carbon next to the carbonyl group. The monoalkali glucopyranose polymer on treatment with a metal or other inorganic salt yields a 2-mono-inorganic glucopyranose polymer.[123]

Hydrogenation of galactose to dulcitol with sodium amalgam is accelerated by addition of lead.[124,125]

The reaction between dialkyl phosphoric acid halides and sodium has been studied by Baudler; the chloride, $(C_2H_5O)_2POCl$, gives $(C_2H_5O)_2OPP(O)(OC_2H_5)_2$ and $(C_2H_5O)_2(O)POP(O)(OC_2H_5)_2$. The compounds $(CH_3O)_2POCl$ and $(C_3H_7O)_2POCl$ and the bromides and iodides behave similarly.[126]

Coloured oily products useful as insecticides and systemic aphicides have been prepared by stirring compounds such as $[(CH_3)_2N]POCl$ and $(CH_3)_2N$-$[CH_3$-(*iso*C_5H_{11})N]-POBr with sodium in toluene at 90° to 95°C.[127]

Phenoxychlorosilicanes, when heated with excess of sodium in boiling xylene, are slowly attacked and a dark bluish-black deposit is formed; the whole of the chloride ion is finally eliminated as sodium chloride, and the filtered solution contains the compound, $Si(OC_6H_5)_4$.[128]

Dichlorides, such as R_2SiCl_2, when heated with sodium yield open or closed-chain structures consisting of $-SiR_2-SiR_2-$ groups; no complex of the type :Si:C: is formed. At about 180°C. in the absence of a solvent, the compound $C_6H_5SiCl_3$ and sodium react slowly but almost quantitatively to give a grayish insoluble powder containing 25·1–26·8%Si; the product does not react with iodine or bromine and is not attacked by piperidine and aqueous alkalies. In boiling benzene or toluene the action of sodium is inappreciable. In boiling naphthalene the reaction with sodium is exothermic and goes to completion more rapidly than in the absence of a solvent. The main product has not been identified but all fractions of it from various solvents contain oxygen; some contain $Si(C_6H_5)_2$ groups and possibly $C_{10}H_7$ radicals. The compound, $C_6H_5SiCl_3$ in boiling benzene or xylene in a sealed tube at 150°C. is fairly readily attacked at first by sodium but prolonged heating is necessary to bring the reaction to completion. The crude product seems to be a mixture of compounds containing from about 6 to at least 50 silicon atoms in their molecules. The components contain not only SiC_6H_5 and $Si(C_6H_5)_2$ groups but also silicon atoms uncombined with carbon; some of the silicon atoms appear to be unsaturated, probably they are tervalent, but most of them become saturated by combination with oxygen.[129]

The following organosilicon compounds have been obtained by the reaction of XCH_2SiRY_2 and $R_3Si(CH_2SiR_2)_xY$ in the presence of sodium, where X is halogen and Y alkoxy or halogen and x is 0 or 1: $(CH_3)_3SiCH_2SiCH_3(OC_2H_5)_2$; $C_6H_5(CH_3)_2SiCH_2SiCH_3(OC_2H_5)_2$; $(CH_3)_3SiCH_2SiCH_3Cl_2$; $(CH_3)_3SiCH_2Si(CH_3)_2$-$CH_2SiCH_3(OC_2H_5)_2$; $(CH_3)_3SiCH_2SiCH_3(OC_2H_5)Cl$. These compounds may be used for the production of other organosilicon compounds.[130]

Hexaphenyldisilane, $(C_6H_5)_3Si$-$Si(C_6H_5)_3$, reacts with sodium in ethylene glycol dimethyl ether to give the sodium derivative, $(C_6H_5)_3SiNa$.[131]

Reactions of sodium with organosilanes at elevated temperatures have been studied by Benkeser and Foster.[132]

Sodium is used for the preparation of butyl tin compounds by a Wurtz reaction.[133] The fungicidal properties of organotin compounds have been described.[134]

Sodium in a highly active state is prepared by passing dry ammonia into a suspension of sodium in toluene (cooled by solid carbon dioxide–ether mixture) until all the sodium is dissolved and then allowing the ammonia to evaporate slowly while the mixture is being vigorously stirred. Powdered sodium produced in this way has been used to synthesize many-membered cyclic oxides and oxidoketones.[135]

Sodium passivated by excessive purity retards organic substitution reactions but the metal may be reactivated by alloying with copper, silver, lead or tin. These metals are converted to amalgams and then alloyed with sodium. The added copper is 0·00002–0·5% of the calculated weight of sodium while the required amounts of silver, lead or tin are double that of copper. Sodium reactivated in this way has been used for Würtz-Fittig reactions.[136]

The handling of sodium in organic reactions and techniques including the use of highly dispersed sodium; of soluble complexes of sodium with ammonia and with the compounds $(CH_3)_2O–C_{10}H_8$, $C_2(C_6H_5)_4$, $(C_6H_3)_3B$; of alloys of sodium with other metals and of primary derivatives of sodium, such as sodium hydride, sodamide, are described by Hansley. Applications in organic chemistry include reduction of aliphatic esters to alcohols, reduction of aliphatic nitriles to primary amines, simultaneous reduction and condensation of esters, refining of hydrocarbons, Claisen condensations such as the self-condensation of ethyl acetate to the ester $CH_3COCH_2COOC_2H_5$. Polymerization and condensation reactions of butadiene are described.[137]

Sodium reacts with triethanolamine to give the sodium derivative, $(C_2H_4OH)_2NC_2H_4ONa$.[138] Ethylphenylethanolamine with sodium yields the sodium derivative $C_2H_5N(C_6H_5)C_2H_4ONa$.[139]

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SECTION XXVI

SODIUM ALLOYS

By MRS. F. DICKINSON

The high thermal conductivity, high specific heat and low density of the alkali metals are properties which make them particularly suitable for use as coolants in heat-transfer systems, for example the removal of heat from nuclear reactors. Liquid sodium and sodium-potassium alloys are now being used on a large scale for this purpose and as a result of this technological interest in the liquid alkali metals a considerable amount of new or revised data for the physical and chemical properties, the flow characteristics, the design of heat-transfer systems and their components, the effect of corrosion on materials of construction, the thermal stress and thermal stress fatigue and the safe-handling of non-radioactive and radioactive liquid metals and alloys as well as methods of fire protection has become available in the literature.[1] A report of the work on liquid metal technology from 1949 to 1954 is given by Werner[2] as has also a general account of sodium-potassium alloys.[3]

Sodium-potassium alloys have now become commercial products. Binary alloy systems of the alkali metals have been studied by Klemm[4] and Böhm and Klemm.[5] Thermal analysis and *X*-ray studies show that the compound Na_2K occurs in the sodium-potassium system. Sodium-potassium alloys, prepared by distillation of the metals, have been used by Rinck[6] to obtain freezing point diagrams. He states that there is an unstable combination, Na_2K, m.p. 6·6°C. and a eutectic melting at -12·5°C. containing 66 at.-% of potassium. A diagram of the liquidus curve from various data is shown in Fig. 1. where the eutectic mixture is seen to freeze at -12·3°C. with 77·2% of potassium by weight.[1] Cryoscopic determinations of the molecular weight of potassium in sodium give a value of 46 which indicates the presence of 18% of diatomic molecules, K_2. The molecular weight of sodium in potassium by the same method is 35.[7] From a study of its crystal structure, the alloy, Na_2K is regarded as a "mixture" of potassium and sodium without special affinities between them. The forces in Na_2K must be about the same as in metallic potassium or sodium; the melting point of 7°C. for the alloy compared with that of potassium and sodium confirms this assumption.[8] An investigation of the sodium-potassium equilibrium diagram has also been made by MacDonald, Pearson and Towle[9] and by Kean[10] and the effect of pressure from 1 to 10,000kg./sq. cm. on the electrical resistance of the liquid phase examined. The rise in melting point with pressure is considerably less for the alloys than for the pure metals.

Henry and Raynor[11] in their work on the cohesion of alloys, show that where the two components of a binary alloy exhibit mutual solid solubility, the wider range of solution should be obtained where the smaller ion is dissolving in the solvent with the larger ion. Calculations made for alloys containing small ions bearing a high charge give good agreement with observed results for binary alkali metal systems; solid solution formation is restricted in all cases except potassium-rubidium, potassium-cæsium and rubidium-cæsium for which extensive ranges of solid solutions exist. The relative magnitudes of the liquidus depression in the system sodium-potassium is accounted for and the composition of the eutectic point interpreted.

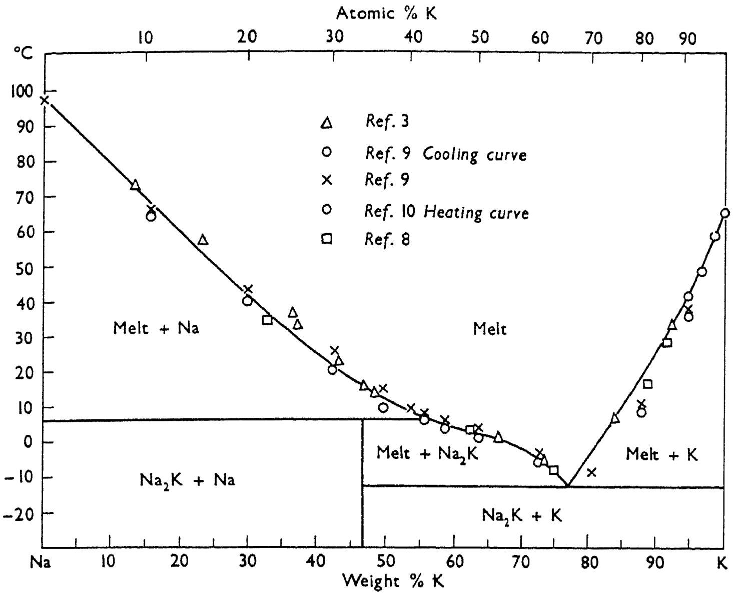

FIG. I. EQUILIBRIUM DIAGRAM Na-K

The following methods have been described for the preparation of sodium-potassium alloys. Freshly cut sodium and potassium are agitated under slightly wet ether.[12] Sodium is heated with potassium chloride above the fusion point of the halide: the salt layer becomes solid at ordinary temperature, while the alloy remains liquid.[13] Sodium vapour is passed in countercurrent through a molten potassium compound such as potassium hydroxide under vacuum and the resultant sodium and potassium vapours are condensed together.[14] Either sodium is heated with potassium hydroxide or potassium with sodium hydroxide and stirred in a well dried steel tube at the equilibrium temperature, 400°C., for 20–30 minutes. The system is rapidly chilled and two phases are obtained, one liquid sodium-potassium alloy (33 at.-% K) the other solid alkali hydroxides. The equilibrium constant for (Na) (KOH)/(K) (NaOH) = 0·5 at 400–700°C. The hydroxide phase contains 18·5% KOH and 81·5% NaOH. If slight carbonation occurs in the handling of the metals before carrying out the reaction, a secondary reaction which is of special importance to the main reaction, occurs:-[15]

$$2Na + K_2CO_3 \rightarrow 2K + Na_2CO_3$$

Clean liquid sodium-potassium alloy is obtained by floating the liquid alloy in a benzene-alcohol mixture and adding solid pieces of clean sodium and potassium until a bright globule of the desired size is obtained. The alloy may be stored under purified kerosene containing less than 0·5% of alcohol.[16] Sodium-potassium alloy is produced on a large scale by the reduction of potassium chloride with sodium at high temperature. Fractional distillation of the alloy may be used to obtain pure potassium.[17] Molten potassium chloride at 1550°F. is fed into the mid-point of a distillation column where it comes in contact with sodium vapour rising countercurrently. The product, a mixture of sodium and potassium vapours, is condensed to the alloy.[18]

Sodium and potassium alloys can be economically and almost quantitatively prepared by fusing sodium at 250–360° with an equivalent amount of caustic potash.[19] The reaction $2Na + KCl \rightleftharpoons Na/K + NaCl$ can also be carried out using potassium fluoride,[15,20] bromide[15,21] or iodide.[15,22] An alloy of sodium with 16·1% of potassium is in equilibrium with a fused salt containing 61·2% of potassium chloride, the remainder being sodium chloride. The mixture corresponds very nearly to the eutectic which melts at 650°C. An account of the equilibria between sodium and fused potassium hydroxide and halides has already been given (see page 478).

Jackson and Werner[23] give an example of the production of sodium-potassium alloy. Molten potassium chloride (1500°F.), 150lb., is charged into a preheated reaction vessel purged with nitrogen and 23lb. of brick sodium added to give a 2:1 mole ratio of potassium chloride to sodium. The reaction vessel and the condenser line are made of stainless steel, the rest of the system being of mild steel. Equilibrium is rapidly established and the more volatile metal phase distils giving a liquid metal distillate containing 47 at.-% of potassium.

The solubility of potassium in sodium is very nearly linear with temperature down to 7°C. and may be represented by the equation:-[1]

$$W = 57{\cdot}1 - 0{\cdot}586t$$

W = wt. %; t = degrees Centigrade.

The values given in Table I for the density of sodium-potassium alloys are taken from the Liquid Metals Handbook[1] which gives references to the sources from which the data have been obtained.

The specific volume of an alloy is obtained from the relation: $V = M(\text{K})V(\text{K}) + M(\text{Na})V(\text{Na})$ where $V(\text{K})$ and $V(\text{Na})$ are the specific volumes, i.e. the reciprocal of the densities, of potassium and sodium respectively, $M(\text{K})$ and $M(\text{Na})$ being the mole fractions of the elements designated. Table I gives both the experimentally determined values for two alloys and the calculated values, and the equation may be used to calculate the density of other alloys with equal accuracy.

TABLE I. DENSITIES OF TWO SODIUM-POTASSIUM ALLOYS

Temp. °C.	43·4% K by wt. Density g./cc.		78·6% K by wt. Density g./cc.	
	Exptl.	Calc.	Exptl.	Calc.
100	0·887	0·890	0·847	0·850
200	0·862	0·867	0·823	0·827
300	0·838	0·843	0·799	0·802
400	0·814	0·818	0·775	0·778
500	0·789	0·794	0·751	0·754
600	0·765	0·771	0·727	0·732
700	0·740	0·745	0·703	0·705

Ewing and Miller[24] prepared five alloys containing respectively, 93, 80, 66, 44 and 33% of potassium and measured their densities over a temperature range of 125°-694°C. For temperatures up to about 200°C. a glass dilatometer was used, but from 300°C. to 700°C. the buoyancy of a copper plunger suspended in the alloy was measured. Selected results are given in Table II.

TABLE II. DENSITY OF SODIUM-POTASSIUM ALLOYS

Composition wt. % K	Temperature °C.	Method	Density g./cc.
93	85·5	Dilatometer	0·8294
–	101·0	Dilatometer	0·8255

continued on following page

TABLE II (continued)

Composition wt. % K	Temperature °C.	Method	Density g./cc.
–	115·5	Dilatometer	0·8219
–	131·0	Dilatometer	0·8180
–	144·0	Dilatometer	0·8138
–	156·0	Dilatometer	0·8116
–	171·4	Dilatometer	0·8114
–	185·0	Dilatometer	0·8081
–	340	Buoyancy	0·769
–	399	Buoyancy	0·752
–	483	Buoyancy	0·733
–	581	Buoyancy	0·714
–	694	Buoyancy	0·689
80	112·3	Dilatometer	0·8442
–	135·2	Dilatometer	0·8385
–	157·0	Dilatometer	0·8328
–	196·7	Dilatometer	0·8225
–	404	Buoyancy	0·768
–	476	Buoyancy	0·756
–	515	Buoyancy	0·747
–	579	Buoyancy	0·732
–	614	Buoyancy	0·724
–	651	Buoyancy	0·716
–	658	Buoyancy	0·715
–	700	Buoyancy	0·702
66	63·6	Dilatometer	0·8656
–	81·0	Dilatometer	0·8609
–	98·6	Dilatometer	0·8559
–	120·0	Dilatometer	0·8523
–	169·1	Dilatometer	0·8447
–	188·3	Dilatometer	0·8391
–	510	Buoyancy	0·760
–	577	Buoyancy	0·745
–	672	Buoyancy	0·721
–	704	Buoyancy	0·719
44	23·8	Dilatometer	0·9119
–	49·8	Dilatometer	0·9029
–	86·0	Dilatometer	0·8937
–	110·3	Dilatometer	0·8816
–	148·8	Dilatometer	0·8717
–	172·0	Dilatometer	0·8658
–	499	Buoyancy	0·7867
–	559	Buoyancy	0·771
–	700	Buoyancy	0·742

Viscosity measurements on sodium–potassium alloys at 125°C. indicate the existence of the compound K_2Na in the liquid state by a maximum on the viscosity/composition curve at 77·2% of potassium. It is assumed that this compound is formed by the decomposition of the disodium compound Na_2K in the potassium-rich range since it does not exist as a solid.[25]

An Ostwald-type viscometer has been used to measure the viscosities of sodium–potassium alloys. The viscosity of an alloy containing 43·4 wt.-% of potassium at 72°C. was 1·267 relative to water at the same temperature. The values at higher temperatures have been calculated from the volumes of alloy flowing per second and the constant determined for the apparatus at 72°C. Measurements are first made on an alloy and water at the same temperature and under the same pressure head. If n_1, n_2, are the viscosities of the alloy and water respectively, d_1, and d_2 the densities, t_1 and t_2 the times required for equal volumes of the fluids to flow then: $n_1/n_2 = d_1t_1/d_2t_2$. From the relative viscosity X and the absolute viscosity of water at the same temperature, the absolute viscosity of the alloy is determined at that temperature. This value with the relation: $n = k/v$ gives a value for the constant k of the apparatus.[24,25] A closed-viscometer technique has been developed for reactive metals with unusually high surface-tension ranges. The values for the viscosity of several alloys from 60° or the m.p. to 200° have been measured and found to range uniformly between those for the pure metals. A 'mixture' equation has been applied to satisfy the data. It has also been shown that the temperature variation of the viscosity values can be adequately expressed by the equation given by Andrade,[27] $nv^{1/3} = Ae^{c/vT}$, where n is the viscosity, v the specific volume, T the absolute temperature and A and c constants for the given liquid.[28] A nickel viscometer of the Ostwald type has been used to substantiate measurements already made at 60° or the m.p. to 200° for sodium, potassium and several alloys to obtain further measurements up to 700°C. The results are given in Table III.[1,29]

TABLE III. VISCOSITY OF SODIUM-POTASSIUM ALLOYS

t °C.	Viscosity in Centipoises	
	43·3 wt.-% K	66·9 wt.-% K
100	0·540	0·529
200	0·379	0·354
300	0·299	0·276
400	0·245	0·229
500	0·207	0·195*
600	0·178*	0·168*
700	0·257*	0·146*

* Based on extrapolation

Values for the empirical constants A and C in the equation $n = p^{1/3} Ae^{Cp/T}$ of three alloys are given in Table IV.

TABLE IV. EMPIRICAL CONSTANTS FOR ANDRADE'S FORMULA

Composition % K	Constants	
	$A \times 10^3$	C
0	1·42	739·8
28·3	1·046	743·3
43·3	1·052	722·3
69·9	1·059	694·0
100	0·9673	716·0

An ideal mixture law for viscosity is considered by Ishikawa[30] to be: $n = n_1 + (n_2 - n_1)\,KZm/(1 - Zm + KZm)$ where n_1, n_2, n denote the viscosities of components 1, 2, and the mixture respectively, Zm the mole fraction of component 2, K a constant which depends on the mutual attraction of the components. The extraordinary values of K in the sodium-potassium system suggest compound formation.

Values for the surface tension of sodium-potassium alloys,[1] obtained from unpublished data from the U.S. Naval Research Laboratory, are given in Table V.

Ewing and Miller[24] report the vapour-liquid equilibria for mixtures of sodium and potassium determined in an apparatus of 18-8 stainless steel. The results obtained are given in Table VI.

TABLE V. SURFACE TENSION OF SODIUM-POTASSIUM ALLOYS

Composition wt.-% K	Surface Tension dynes/cm. (m.p. -250°C.)
56	120 - 110
78	110 - 100

TABLE VI. VAPOUR-LIQUID EQUILIBRIA FOR MIXTURES OF SODIUM AND POTASSIUM

b.p. °C.	Potassium in Liquid Phase		Potassium in Vapour Phase	
	Average Mole-%	Average Wt.-%	Average Mole-%	Average Wt.-%
757	100	100	100	100
778	74·5	83·3	85·9	91·3
796	56·8	69·1	74·5	83·3
814	40·6	53·7	62·5	73·8
835	24·0	34·9	45·0	58·1
858	9·8	15·6	22·8	33·4
882	0	0	0	0

The changes in enthalpy of potassium and three potassium-sodium alloys have been measured at temperatures from 0° to 800°C. with an ice calorimeter.[31] The heat capacities have been derived from enthalpy values, and an empirical equation given to fit the data. For an alloy containing 78·26% of potassium the heat capacity, Cs, in absolute joules per g.°C. at t° is given by the expression: $Cs = 0{\cdot}93860 - 2{\cdot}1924(10^{-4})t + 2{\cdot}1091(10^{-7})t^2 + 0{\cdot}05636(1 - 0{\cdot}0040549t)e^{-0{\cdot}0040549t}$ over the temperature range 0° - 800°C. For an alloy containing 53·64% of potassium $Cs = 1{\cdot}13625 - 5{\cdot}1798(10^{-4})t + 4{\cdot}6266(10^{-7})t^2$ over the temperature range 50° - 800°C. For an alloy containing 44·8% of potassium $Cs = 1{\cdot}16587 - 4{\cdot}3818(10^{-4})t + 3{\cdot}7974(10^{-7})t^2$ over the temperature range 50° - 800°C.

These equations have been used to calculate the heat capacities at the temperatures shown in Table VII.

TABLE VII. HEAT CAPACITIES OF SODIUM-POTASSIUM ALLOYS

Temperature °C.	Heat Capacity	Absolute Joules per g.°C. at t°	
	78·26% K	53·64% K	44·80% K
50	0·9649	1·1115	1·1449
75	0·9523	1·1000	1·1352
100	0·9411	1·0891	1·1259
200	0·9079	1·0512	1·0934
300	0·8882	1·0225	1·0680
400	0·8777	1·0031	1·0514
500	0·8741	0·9929	1·0417
600	0·8759	0·9920	1·0397
700	0·8824	1·0004	1·0452
800	0·8933	1·0810	1·0584

At each temperature from 100° to 800° the heat capacities of the liquid alloys correspond closely to those calculated additively from the values for pure liquid potassium and sodium. As with sodium, each liquid alloy shows a minimum in heat capacity between 500° and 650°C.

The equation $C = W_{Na}C_{Na} + W_KC_K$, where W_{Na}, W_K are the weight fractions of sodium and potassium in the alloy and C, C_{Na}, C_K the heat capacities of the alloy, pure sodium and pure potassium respectively, may be used to calculate the heat capacity of the alloy. Values have been taken from "Liquid Metals Handbook"[1] and are given in Table VIII.

TABLE VIII. HEAT CAPACITIES OF LIQUID SODIUM-POTASSIUM ALLOYS

Temperature °C.	Heat Capacity g.-cal./g./°C.	
	44·8% K	78·26% K
100	0·2690	0·2248
200	0·2612	0·2169
300	0·2553	0·2122
400	0·2512	0·2097
500	0·2489	0·2088
600	0·2484	0·2092
700	0·2497	0·2108
800	0·2529	0·2133

The atomic heat capacities of a sodium-potassium alloy of composition Na_2K have been measured between 12° and 320°K. at constant pressure.[32] Selected smoothed results are given in Table IX where the precision of the results is of the order of 0·1%, and the average deviation of the individual determinations from a smooth curve is 0·06%.

TABLE IX. SMOOTHED ATOMIC HEAT CAPACITY OF Na_2K

Temperature °K.	C_p g.-cal./deg. g. atom	Temperature °K.	C_p g.-cal./deg. g. atom
12	0·304	110	5·671
15	0·583	120	5·771
20	1·193	130	5·860
25	1·847	140	5·937
30	2·454	150	6·001
35	2·984	160	6·061
40	3·416	170	6·120
45	3·791	180	6·181
50	4·123	190	6·243
55	4·394	200	6·316
60	4·611	210	6·402
65	4·798	220	6·498
70	4·959	230	6·601
75	5·094	240	6·711
80	5·215	250	6·828
85	5·319	275	7·407
90	5·409	280·06	7·909 solid
95	5·486	305	8·140 liquid
100	5·553	320	8·012

Data for the region between 280 and 295°K. are not included in Table IX but tests carried out in this region in two series of experiments quoted below show (1) an excess in the heat capacity and (2) discrepancies in the two sets of measurements.

SERIES A		SERIES B	
Temperature °K.	C_p g.-cal./deg. g. atom	Temperature °K.	C_p g.-cal./deg. g. atom
275·89	7·469	282·27	15·973
284·91	15·135	284·17	16·156

continued on following page

continued from previous page

SERIES A		SERIES B	
Temperature °K.	C_p g.-cal./ deg. g. atom	Temperature °K.	C_p g.-cal./ deg. g. atom
288·17	14·833	286·14	16·253
291·55	13·430	288·17	15·996
295·33	11·422	290·42	14·875
299·71	10·085	293·19	12·264
304·50	8·997	296·65	10·408
321·42	7·996	300·87	9·142

In this temperature range, i.e. 280 - 295°K., the stable state of the system is solid sodium plus liquid alloy. Part of the excess heat capacity is probably due to a destruction of local order in the liquid alloy but the greater part seems to be produced by the heat of solution of sodium in the alloy, a process which is undoubtedly endothermal. The discrepancies in the two series of results show that the measurements above 280°K. do not refer to the system in an equilibrium state.

The Na_2K - K eutectic point has been established during the preparation of the alloy of composition Na_2K. The eutectic temperature is found to be -12·65±0·01°C. This may be compared with other values of -12·6, -12·5 and -12·3 reported by Van Bleiswijk,[33] Rinck[6] and Miller, Ewing, Hartman and Atkinson[34] respectively.

The incongruent melting point for Na_2K has been established as 6·90± 0·00°C. Values of 6·90 and 6·6 were obtained by Van Bleiswijk and Rinck respectively.

Entropy changes of the alloy Na_2K for various temperature intervals are given in Table X.

TABLE X. ENTROPY CHANGES OF Na_2K FOR VARIOUS TEMPERATURE INTERVALS

Temperature Interval °K.	Δ *S* e.u./g.-atom
0 - 12 (extrap.)	0·012 ± 0·005
12 - 273·16	12·381 ± 0·009
12 - 280·06 (solid)	12·570 ± 0·010
Phase transformation at 280·06	2·50 ± 0·04
0 - 273·16	12·48 ± 0·02
0 - 280·06 (solid)	12·67 ± 0·02
0 - 280·06 (2 phase)	15·17 ± 0·06
0 - 298·16 (liquid)	16·07 ± 0·03
0 - 320 (liquid)	16·66 ± 0·03

The residual entropy of the alloy Na_2K has been estimated by extending the data in Table X to 420°K. and using the data of Douglas et al.[31] This temperature has been chosen because both metals are liquids and the heat capacity per g. atom is independent of alloy composition. The system thus has one feature of an ideal solution. It is found that $S_{420°K.} - S_{0°K.} = 18{\cdot}74$ e.u./g.-atom. The entropy of $\frac{2}{3}$ g.-atom of sodium and $\frac{1}{3}$ g.-atom of potassium at this temperature is 17·42 e.u. If it is assumed that the entropy of mixing is nearly ideal, $\Delta S_{mixing} = 1{\cdot}27$ e.u./g.-atom. Thus $S_{420°K.}$ for the system is 18·69 e.u./g.-atom which gives a residual entropy of -0·05 e.u./g.-atom. This estimated negative value of the residual entropy suggests that the entropy of formation of Na_2K exceeds the ideal value calculated as the heat of mixing.

The assumption that the heat capacity of the alloy is additively related to the heat capacities of the components is considered to be without theoretical or experimental foundation. In the work cited the deviations from additivity are in some cases quite large and in most cases outside the experimental error.

The estimated residual entropy referred to above should be treated with caution until an experimental value for the entropy of formation of liquid alloy is obtained.

The heats of formation of sodium–potassium alloys have been determined by Kawakami[35] by measuring the heat change when the molten metals are mixed at 110°C.

The value obtained, −48 g.-cal. for 48·7 at.-% of sodium (the maximum point on a Q/x curve, where Q is the atomic internal heat of the mixture and x the at.-% composition) is lower than that given by McKisson and Bromley[36] who also measured directly the heat of mixing. Ketchen and Wallace[37] have determined the heats of formation from the measured heats of reaction of the alloys and the pure metals with water, i.e. the small heats of alloying have been obtained from large heats of solution. For the alloys Na_xK_y, where $x + y = 1$ g.-atom, the heats of formation expressed as g.-cal./g.-atom at 25°C. are 500±90, 820±90, 1150±120, 1100±60 and 800±80 for solid reactants and 60, 260, 590, 550, 230 for liquid reactants, for 37·41, 48·46, 62·10, 68·16 and 78·14 at.-% of potassium respectively.

Average values for the compositions, Na_2K, NaK and NaK_2 given by McKisson and Bromley[36] and considered to be the more accurate values[1,38] are at 25°C. 2130±100, at 110°C. 540±100, at 25°C. 1440±100, at 110°C. 370±100, at 25°C. 2130±100 and at 100°C. 540±100 g.-cal. per g. mole respectively.

The effect of atomic volume on the heat of formation of solid solutions of binary metallic systems has been studied by Heumann.[39] Binding energies are similar between partners which are chemically alike and so contribute little, if anything, to the heat of formation. The heat of formation is largely accounted for by the distortion energy. With the alkali metals, in spite of large volume differences, the distortion energies are small, so that all possible solid solutions are permissible.

A means for evaluating the entropies of fused sodium–potassium alloys is mentioned by Wallace et al. who discuss the applicability of chemical thermodynamics to the study of alloy formation.[40]

Volume increments of compounds for sodium with potassium are given by Biltz and Weibke.[41] The density of the alloy, Na_2K, is 0·8012 at 0°C. from which a corrected value of 87 is obtained for a molar volume. The sum of the atomic volumes is 89 and the compound increment 60.

Kubaschewski and Catterall[38] express the volume change on formation of the alloys by $\Delta V_T = [V \text{ alloy} - \Sigma V(\text{metals})] / \Sigma V(\text{metals})$ at T°. For 1 g.-atom of NaK_2 (i.e. ⅓ g.-mole of NaK_2), $\Delta V_{373} = -0{\cdot}007$ and $\Delta V_{673} = -0{\cdot}0095$. For 1 g.-atom of Na_2K, $\Delta V_{373} = -0{\cdot}010$ and $\Delta V_{673} = -0{\cdot}014$.

The thermal conductivities of two sodium–potassium alloys containing 56·5 and 77·7% potassium have been measured by Ewing, Seibold, Grand and Miller.[42] There is a good analogy between the thermal conductivity-temperature curves and the electrical conductivity-temperature curves. The calculated value of the Lorentz number approaches the theoretical value of $2{\cdot}45 \times 10^{-8}$ watt-ohm/°C.A.

Electrical resistance measurements have been made on alloys containing 44·3 and 80% of potassium by Drugas, Rehn and Wilkinson.[43]

The results obtained for the thermal conductivity and electrical resistance by these workers are cited in Liquid Metals Handbook[1] and given in Table XI.

Table XII gives the electrical resistivity figures reported by Rahiser, Werner and Jackson.[1,44]

The change of resistance of liquid sodium–potassium alloy at room temperature in magnetic fields up to 13,000 gauss has been studied by Fakidov and Kikoin[45] and found to follow a linear law even in weak fields.

TABLE XI. THERMAL CONDUCTIVITY AND ELECTRICAL RESISTIVITY OF SODIUM-POTASSIUM ALLOYS

t°C.	Thermal Conductivity (K) watts/cm.^{2}-°C./cm. 77·7% K	Electrical Resistivity (r) Microhms-cm. 80% K	Lorentz No. $rK/T \times 10^8$
150	0·238	41·6	2·34
200	0·247	44·4	2·32
300	0·259	51·4	2·32
400	0·262	58·8	2·29
500	0·262	67·3	2·28
600	0·259	77·3	2·29
700	0·255	89·3	2·34

TABLE XII. THERMAL CONDUCTIVITY AND ELECTRICAL RESISTIVITY OF SODIUM-POTASSIUM ALLOY 56·5% K

t°C.	Thermal Conductivity (K) watts/cm.^{2}-°C./cm.	Electrical Resistivity (r) Microhms-cm.	Lorentz No. $rK/T \times 10^8$
200	0·249	47·23	2·49
300	0·262	54·33	2·48
400	0·269	62·21	2·49
500	0·271	69·37	2·43

For field strengths (H) greater than 1000 gauss, the relative change of resistance, $\Delta r/r$, with the magnetic field is represented by the equation: $\Delta r/r = aH + b$. This agrees with the results of Kapitza for solid metals but the straight-line portions of the curves start at a higher value of H for the liquid than for the solid state. For a field of 11,400 gauss $\Delta r/r = 6{\cdot}1 \times 10^{-4}$ at room temperatures and $2{\cdot}4 \times 10^{-4}$ at 100°C. The electrical properties of liquid metals are like those of solid metals; therefore conductivity of metals cannot be accounted for by assuming a periodic crystal lattice.[46] The use of very fine containing tubes is believed to minimize spurious effects due to motion in the liquid. The results of Fakidov and Kikoin have been confirmed and in addition it has been found that longitudinal magnetic fields produce a larger effect than transverse fields. For fields over 2000 gauss there is a straight line relationship between magneto resistance and field strength.[47,48]

The change of thermoelectromotive force and electrical conductivity of a sodium-potassium alloy in passing from the solid to the liquid state was investigated by Siebel in 1919.[49] The alloy studied melted at 6·5°C., had a density of 0·8871 at 18°C. and contained sodium and potassium in the ratio of their atomic weights. The thermoelectromotive force was determined against Constantan, one junction being kept at −37·9°, the other at −40° to 40°C. By plotting thermoelectromotive force against the absolute temperature, the slope of the curve below −10°C. is given by $dE/dT = 37 \times 10^{-6}$ volts, above 18° $dE/dT = 35{\cdot}3 \times 10^{-6}$ volts, while around the melting point there are three sharp breaks; the slope at the melting point is 70×10^{-6} volts. In passing from the solid to the liquid state there is a decrease of $1{\cdot}7 \times 10^{-6}$ volts in thermoelectromotive force. The electrical conductivity has been measured between −60° and 40°. Above 18° and below −20° the resistance is a linear function of temperature; the temperature coefficient $a = 0{\cdot}0015$ and 0·0097 respectively. In the region of the melting point, i.e. between 6° and 8°C., a increases rapidly. If the number of electrons in 1 cc. of solid metal is N and the increase in volume during melting is y per c.c. then $N' = N/(1 + y)$ and is the number of electrons in 1 c.c. of liquid metal. As $dE/dT = (2R/F) \log N/N'$ and $\gamma = 0{\cdot}0098$ c.c. then $dE/dT = (2R/F) \log (1 + \gamma)$, which gives the potential difference between solid and liquid metal, $dE/dT = 1{\cdot}68 \times 10^{-6}$ volts, which corresponds closely with the experimental value of $1{\cdot}7 \times 10^{-6}$ volts.

Macdonald and Pearson,[50] have reported on the thermoelectric behaviour of sodium-potassium alloy, Na-K, below 80°K. Of the alkali metals and their alloys with each other, only sodium behaves according to the conventional electron transport theory. According to Domenicali and Otter,[51] the thermoelectric power in a metal depends on the details of how the current carriers in the metal are scattered by the various deviations of the crystal from a perfect lattice; the usefulness of thermoelectricity as a tool for studying the nature of lattice imperfection is briefly discussed. A semiempirical theory of thermoelectric power of metal alloys is described in which the absolute thermopower is related to the energy dependence of the scattering cross section of a lattice imperfection. The correlation with high temperature thermoelectric properties of binary alloys of the alkali metals is quite satisfactory but the low temperature properties cannot be properly discussed without further extensive experiments at very low temperatures.

Because of their relatively low melting points, high boiling points, thermal stability, low vapour pressure and high heat-transfer coefficients, sodium-potassium alloys are particularly suitable as heat-transfer liquids in heat exchange systems. Their pumping characteristics are comparable to those of water but their low specific heats require a larger weight of metal than of water to remove the same amount of heat with the same temperature difference.[1,52,53] They may be used as coolants for nuclear reactor plants and steam generation.[1,52,54,55]

Much of the data collected so far on the performance of sodium-potassium alloy in heat exchange systems has been based on experiments designed for application rather than for acquiring fundamental information and an account of the work so far carried out is given in Liquid Metals Handbook[1] which contains a considerable number of literature references. Heat transfer under various conditions with natural circulation or convection, such as would result owing to temperature gradient in a container, is discussed.

Data and diagrams for specific cases are given with references to the literature.[1] Hyman, Bonilla and Erlich[56] in their work on natural-convection transfer processes at horizontal cylinders deal with the effects of flow patterns resulting from various rates of heat transfer and emphasise the effect of wetting.

Heat transfer with forced convection is also fully discussed and results and diagrams for specific cases are given[1] with many literature references.

Katz[1] discusses heat transfer in a boiling sodium-potassium alloy system. Heat transfer by condensation is discussed with reference to sodium-potassium alloy by Bonilla.[1]

The presence of impurities in sodium-potassium alloy may accelerate corrosion, impair mechanical and thermal performance of equipment and when the alloy is used as a nuclear reactor coolant may induce radioactivity. At oxygen contents above 100 p.p.m. the corrosion rate for many materials is markedly increased; carbon and calcium affect corrosion to a lesser degree but calcium in sodium attacks nickel. There have been no apparent corrosive effects due to the other major impurities in sodium-potassium alloys, e.g. chlorine, lithium and mercury. Owing to the decreased solubility of sodium oxide in sodium-potassium alloy at lower temperatures, the oxide will deposit as a solid whenever the temperature falls below the solubility limit. For this reason the oxygen content should be limited to less than saturation at the lowest system temperature, preferably less than 10 - 20 p.p.m.. It is highly desirable to keep all other insoluble materials to a low value by filtration.

The sources of impurities in sodium-potassium alloy, their effects on the efficiency of the alloy as a liquid coolant, methods of internal and external sampling, analytical techniques for the determination of oxygen, potassium, calcium, carbon, hydrogen, metals other than the alkali metals, purification by filtration, chemical means and distillation are described in detail with many references.[1]

Since sodium-potassium alloy reacts with oxygen and moisture it is necessary to protect the alloy by the use of an inert gas, such as nitrogen, argon or helium. For reasons already mentioned, the inert gas must contain as little oxygen as possible; hydrogen will tend to form hydrides which will result in plugging; water vapour is a source of oxygen and hydrogen; the presence of hydrocarbons in the inert gas results in "cracking" at high temperatures with consequent addition of hydrogen to the system. Also steel will be carburized; at temperatures up to 1000°F. with reasonable amounts of hydrocarbons the carburization will only be of the order of a mil in depth but this might affect certain equipment.

Although nitrogen, argon and helium are not appreciably soluble in sodium-potassium alloy they may be entrained as gas bubbles. Helium alone does not become radioactive but argon on the other hand has a substantial cross section and emits beta and gamma radiation with a half life of 1·82 h. Nitrogen is better than argon owing to the short half life of 7·3 sec. for ^{16}N.

A reactor coolant system becomes radioactive as a result of reactor operation. The radioactive material in the system will emit both gamma and beta rays but nearly all the beta radiation will be absorbed by the pipe walls. Kendall and Grand discuss the radioactive material transfer which occurs in reactor coolant systems.[1]

Fleischmann and Koenig[1] give an account of the factors which must be taken into account when choosing materials of construction and methods of fabrication for sodium-potassium coolant systems.

Since there is little thermal resistance in the liquid alloy film, the total temperature difference between the liquid alloy temperature and the temperature on the other side of the wall of the containing vessel occurs within the dividing metal wall causing stresses due to differences in thermal expansion proportional to the temperature difference. The maximum thermal stress decreases with increasing thermal conductivity of the structural material and increases with increasing surface heat transfer coefficient and wall thickness.

Another important factor in the design of a heat transfer system using sodium-potassium alloy as a coolant is the resistance of the structural materials to corrosion. A choice has to be made between corrosion-resistant materials having low thermal conductivity and high coefficients of expansion, and the less corrosion-resistant materials with better thermal properties. Fatigue failure of structural materials must also be considered because of the severe thermal stress involved. All these points as well as safety and fire precautions are discussed in detail.[1]

The measurement of heat-transfer coefficients in a double annulus heat exchanger with sodium-potassium alloy as coolant has been carried out by Hall and Jenkins.[57] The performance of small liquid sodium-potassium heat exchangers has been assessed by Tidball.[58] Trocki and Bruggeman[59] give an account of the use of sodium-potassium alloy for reactor cooling and steam generation and discuss the heat transfer, chemical and corrosion effects and describe the pumps, valves and instruments used in the system. Trocki, Bruggeman and Crever[55] describe fluid handling of sodium-potassium alloy for reactor cooling and steam generation. Many other papers also deal with the subject[60-64;52-54] and with pumping systems for liquid sodium-potassium alloy.[65-68]

Corrosive effects of sodium-potassium alloy on various materials at high temperatures, i.e. up to 800°C., have been studied by Kelman.[69] Uranium, thorium, beryllium and niobium show extremely good resistance; the presence of oxygen in the alloy affects the corrosion resistance of these metals adversely. The presence of chromium and high-chromium alloys greatly accelerates the attack upon steel by sodium-potassium alloy. Nickel and high-nickel alloys show extremely good resistance. Generally copper and its alloys, carbon, silicon, silver and platinum are extensively attacked by sodium-potassium alloy. The corrosion of low alloy steel in hot sodium-potassium alloy has been studied by Milich and King.[70] Specimens of AISI 347 pipe and pipe welds have been subjected to repeated thermal shocks by quenching the inner surface with cool sodium-potassium alloy; it would appear to be safe to use current design methods where stresses caused by thermal shock are not in excess of those reported by Tidball and Shrut.[71]

The use of sodium-potassium alloys as coolants in arc and vacuum melting in titanium metallurgy is discussed by Cooper and Herres;[72] the alloys do not explode when in contact with molten titanium. The term "advantage factor" is used by Convey[73] to compare various coolants for use in atomic reactors: the "advantage factors" of water, liquid sodium, 78% potassium-22% sodium eutectic, liquid lead, liquid bismuth and liquid lithium are $3{\cdot}3 \times 10^4$, $2{\cdot}3 \times 10^{13}$, $2{\cdot}4 \times 10^{11}$, $1{\cdot}3 \times 10^{10}$, $4{\cdot}6 \times 10^{14}$, and $5{\cdot}0 \times 10^{14}$, respectively.

An alloy of sodium and potassium, liquid at -12°C. may be moved by a magnetic field acting on it while it is traversed by an electric current and use is made of this property in pumping or compressing systems such as those of refrigerators.[74]

The thermal, chemical and radiation hazards of liquid sodium-potassium alloy are reviewed by Finkel and Lyons.[75]

The results of some 'wetting' tests are given in Table XIII. During the lowering of the sample to make contact with the specified metal the meniscus between the alloy and the metal is observed and the temperature at which the metal surface is 'wetted', noted. A depressed meniscus is recorded as not 'wetting' whereas a flat or raised meniscus at the metal surface is described as 'wetting'.[24]

TABLE XIII. 'WETTING' OF METAL SURFACES BY SODIUM-POTASSIUM ALLOY

Metal Surface	Temperature of 'Wetting' °C.		
	30% wt. K	45% wt. K	65% wt. K
Soft Iron	270	295	310
Stainless Steel	260	290	320
Nichrome	320	330	340
Nickel	345	320	350

The X-ray diffraction haloes exhibited by different proportions of sodium and potassium in sodium-potassium alloys have been studied by Banerjee.[76] The alloys are regarded as solutions of an excess of sodium or potassium in the liquid compound Na_2K. When the amount of dissolved metal is small the halo is nearly the same as that of Na_2K; when one of the metals preponderates the halo is practically that of the preponderant metal. Alloys of intermediate composition give haloes in which the effects of the excess metal and the compound Na_2K are superimposed. It appears that the three atoms in the compound Na_2K are situated at the corners of a triangle. A faint inner ring is observed where the excess of either metal is small.

Monochromatic X-ray diffraction patterns of liquid sodium-potassium alloys at 115°C. have been prepared by Gingrich and Henderson and plots of position of main peak versus composition constructed. There is no indication of the inflexion attributed to Na_2K molecules in the liquid by previous work.[77]

Heaps[78] has shown that the intensity of *X*-ray scattering by liquid sodium-potassium alloy is not changed by as much as 2% in a field of 2700 gauss. There is no volume change of as much as 3×10^{-7} in a field of 7800 gauss. The increased resistance in a magnetic field found by Armstrong[47] cannot be due to changes in molecular grouping.

The optical constants of sodium-potassium alloys containing 11 - 76% of potassium have been measured by Morgan.[79] For an alloy of composition NaK the refractivity is at a maximum value of 0·137, the absorptive index at a minimum value of 12·5. A change in temperature causes a change in optical constants for some of the alloys but not for all.

In Table XIV n and κ refer to the mean values of the index of refraction and index of absorption for green light 5461A. and are considered to be within 10% of the true values. The reflecting power R has been calculated from the mean values of n and κ. The index of refraction is from air to water.

TABLE XIV. OPTICAL CONSTANTS FOR SODIUM-POTASSIUM ALLOYS

Wt.-% K	At.-% K	n	κ	R
17·3	11·0	0·081	27·2	94·6
36·2	25·1	0·100	18·5	91·4
45·0	32·5	0·108	16·8	90·4
55	41·8	0·115	15·6	89·7
66	53·3	0·137	12·5	87·0
74·2	62·7	0·124	12·8	86·9
84·3	76·0	0·088	17·6	90·2

Although there is a marked change in n and κ for the solid alloy containing 82·7% Na and 17·3% K on increase of temperature, it is probably due to the process of fusion since the optical constants for the liquid alloys appear to be unaffected by change in temperature.

Kent[80] has used the optical data of Morgan to compute for sodium-potassium alloys the number of free electrons per atom and the frequency of impact of the free electrons with molecules. The number of free electrons per atom is found to be 1·5 for most alloys with a value of 1·2 for NaK_2. The frequency of impact of the free electrons with molecules is of the order of $1-3 \times 10^{14}$ per second; it increases linearly with the increase in percentage of either constituent to a maximum for the compound NaK. Resistivity computed from optical data agrees within experimental error with experimental data for two of the alloys.

The existence of intermetallic compounds in the vapour state has been shown by a study of the spectra of the alloys of the alkali metals with each other. The observed bands for the molecule, NaK, lie near the principal series lines of the constituent atoms.[81]

Calculation of the dependence of the lattice constant of binary solid solutions on the composition is described by Orlov,[82] and an expression is derived for solid solutions of the alkali metals.

In agreement with the most frequently observed behaviour, the theory predicts a growth of the lattice constant with increasing concentration (at low concentrations) of the metal with the smaller radius.

Electrolysis of sodium-potassium alloy has been studied by Kremann and Rehenburg.[83] An alloy containing 70% of potassium and 30% of sodium, liquid at room temperature, is placed in a 1 mm. capillary tube and electrolyzed at 100°C. using copper electrodes at a maximum current density of 7·2 amp./sq. mm. At the end of 4 hr. the capillary is cooled, broken up into lengths and analysed. The concentration of sodium is found to increase at the anode, that of potassium at the cathode. The percentage difference in composition increases with current density, the increase in potassium concentration at the cathode being 10% at 1·4 amp./sq.mm. 24·5% at 4·45 amp./sq.mm. and 32·15% at 7·17 amp./sq.mm.

Photoelectric emission in sodium-potassium alloys has been studied by Ives and Stilwell.[84] The entire series of alloys has been investigated with respect to the relative values of the photoelectric currents produced by light polarized with the electric vector in and at right angles to the plane of incidence. The pure molten metals give values below 3 for the ratio of the two emissions; the alloys give three maxima at 20, 50 and 95% sodium with values of 10–30 for the ratio of the two emissions; the low values of the minima between the peaks approximate to those for the pure metals.

Emission of electrons by sodium-potassium alloys under the influence of chemical action is described by Richardson et al.[85-89] The alloys are subjected to the action of phosgene, chlorine, water vapour, nitrosyl chloride, carbonyl sulphide, bromine, iodine, thionyl chloride, sulphur chloride, sulphuryl chloride and mercuric chloride at low pressure when electrons are emitted. Energy distribution curves are given at pressures in the range of 10^{-6} to 10^{-3} mm.; with hydrogen chloride and water the emission is small but probably real; with nitrous oxide it is very small and probably zero. Current and pressure curves are given for chlorine, nitrosyl chloride, carbonyl sulphide, current and time curves are given for chlorine. Maximum electron energies are equal to the difference between the chemical energy available in the reaction and the work function of the alloy if the reactions with chlorine, nitrosyl chloride, or phosgene occur in one stage and with bromine and iodine in two stages: $M + COCl_2 \rightarrow 2Cl^-$ adsorbed on M + (CO); $M + (NOCl) \rightarrow Cl^-$ adsorbed on M + (NO); $M + Cl_2 \rightarrow 2Cl^-$ adsorbed on M; $M + Br_2 \rightarrow Br^-$ adsorbed on M + (Br); $M + (Br) \rightarrow Br^-$ adsorbed on M; $M + I_2 \rightarrow I^-$ adsorbed on M + (I); $M + (I) \rightarrow I^-$ adsorbed on M. It is assumed that a polar bond is first formed and stabilized with a three-body collision with the free metallic electron which then carries away the surplus reaction energy. These experiments may have some importance in connection with the kinetics of heterogeneous chemical reactions.

Sodium-potassium alloys are generally more reactive than sodium. Whereas sodium is oxidized at room temperature to sodium monoxide, potassium oxidizes finally to the superoxide, KO_2. The oxide which precipitates from solution in sodium-potassium alloys at 200°C. is however entirely sodium monoxide.[1] Oxygen may be removed from commercial hydrogen, nitrogen and argon by passing the gas through a trap containing liquid sodium-potassium alloy, 25% Na, 75% K. Water vapour may also be removed in this way.[90,91] The solubility of oxygen in sodium-potassium alloys approximates to the ideal value in the temperature range 20°–176°C. but the partial heat of solution changes at 260°–270°C.[92] Oxygen may be determined in sodium-potassium alloy by the butyl bromide method for determining oxygen in sodium, with certain modifications.[93]

Vapour phase combustion of sodium-potassium alloy containing 60% potassium yields a mixture of sodium peroxide and potassium superoxide, KO_2, commonly referred to as "MOX."[94]

Sodium-potassium alloys containing 25–90% of potassium, which remain liquid at room temperature and are ordinarily oxidized readily on exposure to air, may be kept as lustrous alloys in sealed tubes by the procedure earlier described for sodium (see page 460).[95]

The reaction of sodium-potassium alloy with water in the presence or absence of oxygen has been carried out by rapidly mixing the reactants by applying pressure to pistons and forcing the reactants through two opposing jets into the mixing chamber. An improved apparatus capable of contacting 1 ml. of each reactant in 2 msec. has been described. In the presence of oxygen two pressure waves are observed by a pressure-recording system. When the excess of water relative to alloy is reduced sufficiently, ignition occurs and only one maximum corresponding to the second pressure wave is observed. Only the first pressure wave is recorded when oxygen is absent.[96]

Ketchen and Wallace[37] give the heats of reaction of sodium–potassium alloys with water reproduced in Table XV: Alloy (l) + ∞H_2O = mixed hydroxides (∞H_2O) + $0{\cdot}5H_2$.

TABLE XV. HEATS OF REACTION OF Na–K ALLOYS WITH WATER AT 25° C.

At.-% K	$-\Delta H^\circ_{298}$ g.-cal./g.mol.
37·41 ± 0·06	45,190 ± 70
48·46 ± 0·10	46,550 ± 80
62·10 ± 0·07	47,260 ± 100
68·16 ± 0·14	47,390 ± 40
78·14 ± 0·29	47,370 ± 60

The half-time of the reaction between sodium–potassium alloy and ethyl alcohol is found to be several milliseconds. The reaction is carried out in an apparatus especially designed for the measurement of the rates of rapid reactions; a constant volume bomb with provision for rapid mixing is used and the progress of the reaction is observed by pressure changes using a strain gauge and a cathode-ray oscilloscope.[97]

When an electric discharge is passed through nitrogen and hydrogen, with sodium–potassium alloy present in the discharge tube either as cathode or anode, absorption of the gases takes place. Similar absorption occurs when the gases are ionised by alpha rays from polonium. The formation of nitrides and hydrides has been proved by chemical analysis. With nitrogen the effect of increase of temperature up to 200° C. is nil but above this temperature absorption increases.[98,99]

The apparatus used by Newman[98,99] for the absorption of hydrogen by sodium and potassium in the electric discharge tube has been modified in order to increase the amount of gas absorbed so that the amount of the reaction products would be sufficient for analysis. At a temperature of −40° C. and a voltage of 600 volts a thin white crystalline coating is formed on the surface of the alloy but as the reaction continues the coating becomes dark grey. A mixture of sodium and potassium hydrides is formed. The black deposit, earlier attributed to the hydrides, has now been shown to be a mixture of suboxides of sodium and potassium. Water is considered to be formed from the glass during the passage of an electric discharge through a vacuum vessel and is not wholly retained by a trap at −40° C. since the vapour pressure of water at this temperature is 0·1 mm. Hg. The black deposit fouling the surface of the alloy is quite unlike the white crystalline layer of sodium and potassium hydrides.[100]

Sodium–potassium alloys are especially sensitive to impact with tri- and tetra-chloromethane, tribromomethane and tetra- and penta-chloroethane. The last three halogen compounds and sodium–potassium alloy have been known to explode even on standing at ordinary temperatures.[101] The explosive action of sodium–potassium alloy on detonation with methyl chloride, methylene chloride and chloroform is described by Staudinger as moderately strong, strong and very strong respectively.[102]

Cueilleron[103] has shown that a mixture of sodium or potassium and a halide of a metal or metalloid (except those of the alkali or alkaline earth metals) explodes when subjected to shock by striking with a hammer. Explosive reactions also occur in general with oxygen-containing compounds (see page 497). The power of the explosion decreases in the order: sodium–potassium alloy, potassium, sodium, lithium, barium.

Sodium–potassium alloys react explosively with solid carbon dioxide;[104,105]

violent reactions also occur with water, carbon tetrachloride, sodium bicarbonate and foam type extinguishers. In no case should a can sealed with solder be used to contain sodium-potassium alloy.[105]

A violent explosion occurs when oxalyl chloride or bromide is treated with sodium-potassium alloy.[106]

Reactions of sodium-potassium alloy with alkyl halides are described by Hückel, Kraemer and Thiele.[107] Methyl bromide and sodium-potassium alloy in xylene give 12·5% ethane; ethyl bromide gives 28% ethane and 40% butane; a mixture of methyl and ethyl bromides in xylene with the alloy at 20°–30°C. yields ethane, ethylene, propane and butane. Propyl bromide under the same conditions gives 8–11·5% of propane, 6–7·5% of propene and 55–65% of hexane. A mixture of methyl bromide and propyl bromide in xylene with sodium-potassium alloy yields ethane, propene, butane and hexane. *iso*Propyl bromide is converted to 45% of propane and 10% of propene; a mixture of methyl bromide and *iso*propyl bromide gives ethane, propene and *iso*butane. *iso*-Propyl bromide and sodium-potassium alloy in decalin are converted to 27·5% propane and 25% propene; in benzene solution 40% of propane and 31·5% of propene are obtained. Methyl chloride does not react with sodium-potassium alloy in xylene; ethyl chloride gives 20·5–32% of ethane, 2–5·5% of ethylene and 3·3–16% of butane. *iso*Propyl chloride and sodium-potassium alloy in xylene give 45% of propane and 10% of propene.

The action of sodium-potassium alloy on aliphatic, aromatic and mixed ethers has been studied by Durand.[108] The liquid alloy reacts more vigorously than sodium, particularly in the cold.

Sodium-potassium alloy attacks silicon;[1] a crystalline substance, NaSi, is formed which inflames in air; if heated under reduced pressure the compound decomposes into sodium and silicon.[108a]

Reactions of organosilanes with sodium-potassium alloy are described by Benkeser et al.[109] Diphenylsilane, Ph_2SiH_2, and monophenylsilane, $PhSiH_3$, react with sodium-potassium alloy by a mechanism different from that ascribed to the reaction of triphenylsilane, where the reactive intermediate is Ph_3SiK. Examples of the reactions are given.

Hexaphenyldisilane is readily cleaved by sodium-potassium alloy in glycol dimethyl ether, $(CH_2OCH_3)_2$ and the potassium derivative formed, Ph_3SiK, is soluble in glycol dimethyl ether but insoluble in ether.[110]

The dimethyl ether of ethylene glycol, when treated with sodium-potassium alloy, is found to contain sodium in solution.[111]

The reduction of titanium tetrachloride with sodium-potassium alloy has already been mentioned (see page 492).

The conductivities of sodium and potassium in dilute liquid ammonia show no evidence of compound formation between the metals.

Conductivities and solubility relations in the ternary system, $Na\text{-}K\text{-}NH_3$, have been given for the range -40° to +70°C.[112]

The carbon content of sodium-potassium alloys is determined by igniting a 100 mg. sample in oxygen and absorbing and weighing the carbon dioxide formed. The procedures for sampling the hot alloy from a dynamic system, and transferring the sample to specially designed analytical equipment have been described.[113,114]

To obtain solutions of sodium-potassium alloys for analysis the alloys may be frozen in a borosilicate glass dish on solid carbon dioxide and then added to a slurry of alcohol and solid carbon dioxide[115] or the alloy may be placed in a beaker and blanketed with helium or argon, using an inverted funnel for the purpose, and *n*-hexane added to cover the alloy which is then treated drop-wise with methyl or ethyl alcohol.[116]

The partial pressure of mercury vapour in a vacuum tube may be reduced to 10^{-5}, (or by using special diaphragms to 10^{-6} mm. Hg) by means of sodium-potassium alloy (30:1) as a getter. The alloy is vapourised in a vacuum to condense on a surface and is found to capture 30% of vapourized mercury molecules with practically no impairment of the activity after a fair amount of compounds have been formed on the surface.[117]

The system sodium-potassium-mercury has been examined by Jänecke[118] and constitutional diagrams prepared. The double compound, NaKHg, m.p. 188°C., has been isolated and crystallized in the form of blue, glistening hexagonal prisms.

Halla[119] has calculated the free energy of formation from the ternary phase diagram of the system Na-K-Hg for the reaction: $NaKHg_2 \rightarrow NaHg + KHg$ and gives values of ΔF° at 100° and 150°C. respectively as 809 and 856g.-cal./mole.

An equation has been used by Wagner[120] to determine the change in activity of metal 2 dissolved in metal 1 due to the addition of a solute metal 3. It is necessary that the changes in the activity coefficients with composition for the binary systems 1-2 and 1-3 be known, and that the interaction between positively charged metal ions is of minor importance as compared with the effects due to a change in the chemical potential of the electrons. The system sodium-potassium-mercury has been studied. In the binary system Hg-Na, $d\ln\gamma_{Na}/dx_{Na}$ has been found from the literature to be 36·0, where γ refers to the activity coefficient and x the molar fraction. In the binary system, Hg-K, $d\ln\gamma_K/dx_K = 67{\cdot}0$, $d\ln\gamma_{Na}/dx_K = d\ln\gamma_K/dx_{Na}$ from which:-

$$d\ln\gamma_{Na}/dx_K = \pm\left[\frac{d\ln\gamma_{Na}}{dx_{Na}}\cdot\frac{d\ln\gamma_K}{dx_K}\right]^{1/2}$$

and the calculated value for $d\ln\gamma_{Na}/dx_K$ is therefore 49·1. A study of the reaction: $Na(\text{in Hg}) + K^+(\text{aq.}) = K(\text{in Hg}) + Na^+(\text{aq.})$ by other workers gives an experimental value of $d\ln\gamma_{Na}/dx_K = 46{\cdot}5$.

The compound KCd_3 in the form of needle-like crystals, m.p. >550° is indicated in the system Na-K-Cd-Hg.[118]

The sodium-rubidium system has been described by Rinck,[121] Goria,[122] Böhm and Klemm[5] and Klemm.[4,123]

The solidification diagram for sodium-rubidium shows the absence of solid solutions and of compound formation; there is no compound, Na_2Rb, analogous to Na_2K in the sodium-potassium system. A eutectic occurs at 75 at.-% of rubidium at -4·5°C.,[121] -5·2°C.[122] Although the curve tends to become horizontal in the vicinity of the composition corresponding with Na_2Rb, neither thermal analysis nor *X*-ray studies have indicated that such a compound exists. The solubility of rubidium in sodium is given approximately by the expression $W = 132{\cdot}2 - 1{\cdot}356t$ down to 61°C., i.e. 50% rubidium,[1] where W = wt. % and t degrees Centigrade.

The relative magnitude of the liquidus depressions in the sodium-rubidium system has been accounted for and the composition of the eutectic interpreted by calculations made by Henry, Jaswon and Raynor in their work on the cohesion of alloys.[11]

Determinations of the molecular weight of rubidium by cryoscopic measurements in sodium give a value of 104 indicating that 22% of diatomic rubidium, Rb_2, is present; sodium in rubidium is monatomic.[7]

Thermal neutron absorption cross sections of rubidium are significantly lower than those for potassium; sodium-rubidium alloys would in this respect be especially suitable as coolants for atomic reactors. The macroscopic physical properties of these alloys are similar to those of sodium-potassium alloys.[124]

The phase diagram[125,126] is shown in Fig. 2.

The sodium-cæsium system has been described by Rinck,[7] Böhm and

Klemm,[5] Goria[127] and Klemm.[4,123] Thermal analysis shows a eutectic at −30°C. and at 75 at.-% of cæsium, a transition point at −8°C. and 71 at.-% of cæsium, and an indication of the compound Na_2Cs.

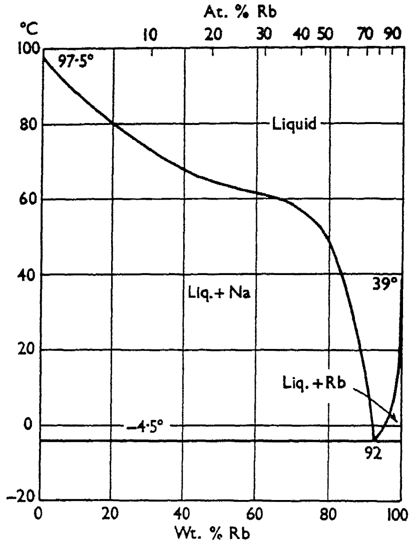

FIG. 2. EQUILIBRIUM DIAGRAM Na–Rb

The volume contraction on alloying is less than 5%.[5] The magnetic susceptibility of the alkali metal alloys has been measured at various temperatures and the formation of compounds or mixed crystals in the sodium–potassium, sodium–cæsium and potassium–cæsium systems is found to decrease the magnetic susceptibility.[5] Henry and Raynor[11] in their work on the cohesion of alloys state that for cases of mutual solid solubility of the two components of a binary alloy, the wider solution should be formed where the smaller ion is dissolving in the solvent having the larger ion. The possible effect on solid solubility relations of the mutual distortion of the electron clouds of the component ions is considered. Calculations made for the alloys of the alkali metals give results in good agreement with the experimental data and show that solid solution formation is restricted in all the possible systems except potassium–rubidium, potassium–cæsium and rubidium–cæsium. The relative magnitudes of the liquidus depression in the sodium–cæsium system and the composition of the eutectic are accounted for. Cæsium lowers the melting point of sodium, and the solubility as wt.-% of cæsium in sodium up to 50% of cæsium (80°C.) is given approximately by the expression: $W = 223 - 2{\cdot}29t$ where t is the temperature in degrees Centigrade.[1]

Cryoscopic measurements in sodium to determine the molecular weight of cæsium give a value of 218 indicating the presence of 64% of cæsium in the diatomic form Cs_2. Sodium in cæsium is monatomic.[7]

The phase diagram[125,126] is shown in Fig. 3.

Copper has been recrystallized from sodium at 550°C. The resistance of copper to sodium is good up to 300°–400°C.[1] but it is not recommended as a constructional material for sodium-handling equipment for permanent usage.[128] No indication of the existence of a copper–sodium compound is given when a solution of sodium in liquid ammonia is titrated with a solution of copper iodide in liquid ammonia. A black precipitate of metallic copper is formed with perhaps a slight amount of sodium, and the supernatant liquid is decolourized.[129] A violent reaction occurs when sodium is used to reduce liquid copper containing 1·35% oxygen at 1150°C.[130]

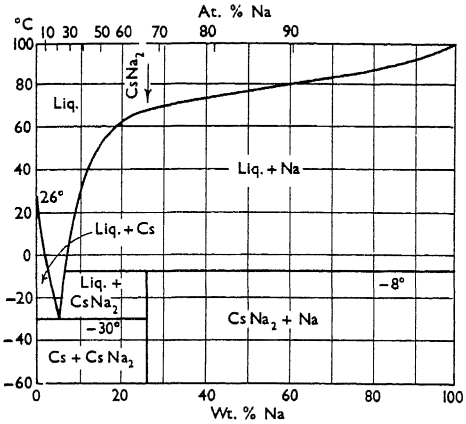

FIG. 3. EQUILIBRIUM DIAGRAM Na-Cs

Sodium is miscible with silver in all proportions. The solubility of silver in sodium up to 650°C. (40% Ag) is given as wt.-% by the expression: $W = -2{\cdot}4 + 0{\cdot}0180t + 7{\cdot}007 \times 10^{-5}t^2$, where t is the temperature in degrees centigrade.[1] Zintl and Brauer[131] by melting together silver with 50 at.-% of sodium obtained a very inhomogeneous alloy with the low hardness of metallic sodium. The reactions of silver salts in liquid ammonia solutions of sodium have been studied by potentiometric titrations, (see page 514). No compound of silver and sodium is formed but silver is precipitated from solution.

Reactions at high temperatures between air and liquid metal solutions containing sodium have been studied by ejecting the heated alloy downward through a small orifice into a large steel chamber previously evacuated and filled with dry air. The amount of oxygen present is 3–30 times that required for complete oxidation of the sodium present and the time of flight of the jet so short that only a fraction of the sodium present can react. The sodium-silver system containing 0·1 mole fraction of sodium in dry air at 700°C. is quite reactive.[132]

The phase diagram[125,126] is shown in Fig. 4.

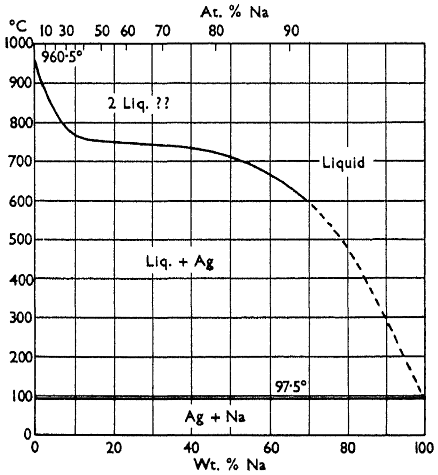

FIG. 4. EQUILIBRIUM DIAGRAM Na-Ag

Gold is miscible with sodium in all proportions; the eutectic containing 22·5% of gold melts at 82°C. The experimental data are represented by the expression: $\log(1 - W/100) = 2{\cdot}5094 - 930{\cdot}25/T$ from the m.p. of sodium down to the eutectic where W is the wt.-% of gold in sodium and T the temperature in °K.[1]

Potentiometric titrations of a solution of sodium in liquid ammonia with a solution of gold iodide in the same solvent show a point of inflexion shortly after the solution is decolourized when the composition of the mixture corresponds to NaAu. Towards the end of the titration a slow steep rise of the potential marks the separation of free gold.[129]

The compound $NaAu_2$ is shown in the phase diagram Fig. 5.[125] Quadt, Weibke and Biltz[133] have obtained the compound $NaAu_2$ by heating fine gold powder with sodium at 250° under high vacuum for several hours in a tube previously filled with argon. Excess sodium is distilled off at 300°–460°. The compound $NaAu_2$ is a bright brass yellow in appearance, stable in air but decomposing slowly at 700°C. An X-ray spectrum has been obtained: the compound crystallizes in the cubic system with 24 atoms per unit cell; a = 7·79A. Perlitz and Aruja[134] give a value of 7·7874 ± 0·0002A. at 20°C. for the side of the elementary cube of the compound $NaAu_2$ and 7·770A. for the side of the cube of the alloy Au(85·7) Na(14·3).

The spatial compression of sodium on combination with gold has been studied by Biltz et al[135] in view of the great differences in the densities of the metals. The space occupied by the alkali metals in their alloys with gold is much less than that occupied by the pure metals; this is regarded as being due to compression.

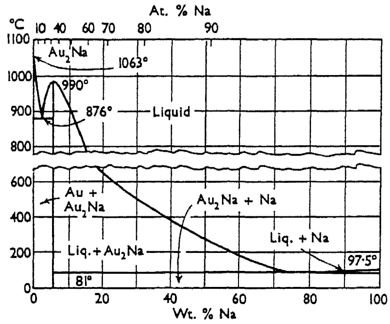

FIG. 5. EQUILIBRIUM DIAGRAM Na–Au

When sodium combines with gold to form aurides, the increase in molecular volume per atom of sodium is only 16· whereas in alloys of sodium with mercury, tin, lead, cadmium the volume increment for sodium is 17.

Beryllium alloys have been prepared by treating molten copper, nickel, iron or aluminium with an alkali metal and with a double fluoride of beryllium and an alkali metal.[136] Beryllium chloride, dissolved in sodium chloride to reduce evaporation losses, is reduced with sodium in the presence of aluminium to give alloys containing up to 10% of beryllium.[137]

Magnesium alloys to a very slight extent with sodium.[138] The magnesium sodium eutectic lies very close to the pure sodium end of the phase diagram; the solubility of magnesium in sodium expressed as wt.-% is given approximately by the expression: $W = -0{\cdot}27 + 0{\cdot}002775t$ up to 700°C., i.e. 1·67% of magnesium.[1] From the phase diagram given in Fig. 6[125,126] the solidifying point of magnesium is seen to be lowered by 2% of sodium to 638°–640°C.; the composition of the sodium-rich melt in equilibrium with the 2% melt and magnesium at 638°C. has been shown by analyses to be 98·5% sodium.

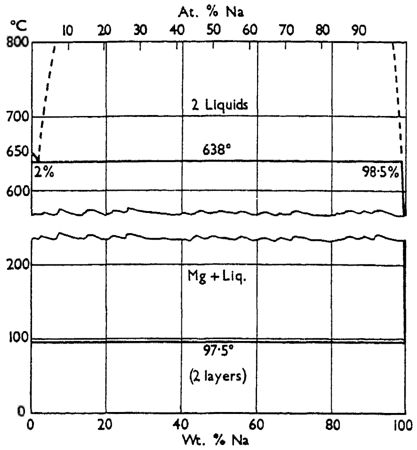

FIG. 6. EQUILIBRIUM DIAGRAM Na-Mg

Calcium-sodium alloys, obtained as a by-product in the Downs cell, can be converted into free sodium and calcium-magnesium alloys by heating with magnesium.[137] Sodium reduction of fused calcium chloride in the presence of magnesium under a protecting atmosphere results in the formation of magnesium-calcium alloys: $2Na + CaCl_2 + Mg = Mg/Ca + 2NaCl$.[139]

The influence of sodium on the mechanical properties of magnesium alloys is discussed by Lugaskov.[139]

Calcium is only partially miscible with sodium; the solubility of calcium in sodium up to 700°C., i.e. 9·4% calcium, is represented by the expression: $\log W = 2{\cdot}5629 - 1545{\cdot}6/T$ with a probable error of ±0·14% where W is the wt.-% of calcium in sodium and T the temperature in °K.[1]

Equilibria in fused salts, $Ca + 2NaCl \rightleftharpoons CaCl_2 + 2Na$, in which the metal phase consists of sodium-calcium alloys, have already been discussed in detail (see page 405). As sodium and calcium chlorides are insoluble in the metal phase, the presence of a salt phase in equilibrium with the metal phase has no influence on the composition of the latter.

Jellinek and Wolff[140] have examined the reaction of fused calcium and sodium chloride in a fire-brick crucible containing molten antimony or bismuth as electrode metals. If at.-% of metal is plotted as ordinates and mole % of its chloride as abscissae then: $x(1 - y)/(1 - x)y = k$. The equilibrium $Ca + 2NaCl \rightleftharpoons 2Na + CaCl_2$ is independent of temperature, cathode metal and even of the presence of water.

Lorenz and Winzer,[141] using pure sodium and calcium containing 1·2% of impurities, made up chiefly of silica, alumina and iron oxide, heated the elements in sealed steel bombs to avoid formation of calcium nitrides and hydrides and found that the limit of solubility of sodium in liquid calcium at 700°C. was 16 at.-% sodium and that of calcium in liquid sodium 0·8 at.-% calcium. Pure sodium was found to freeze out from all alloys studied at 97°C.

Rinck[142] has prepared a solidification diagram of calcium-sodium alloys and criticized the work of Lorenz and Winzer. The m.p. of calcium used by Lorenz and Winzer is given as 809°C.; it has been shown by Antropoff and Falk[143] and also by Rinck[142] that the presence of very small quantities of nitrogen lowers the m.p. of calcium considerably and that the true m.p. of pure calcium is in fact 851°C. (848° for sublimed calcium).

The solidification diagram is shown in Fig. 7 and the experimental results in Table XVI.

The liquidus shows a horizontal branch *a*-*a*'. Calcium and sodium are thus reciprocally miscible for mixtures containing between 4 and 77 at.-% of calcium. The composition of the heavy layer at 712°C. i.e. of the saturated solution of sodium in calcium at *a*′ is 77 at.-% of calcium. The composition at point *a*, i.e. saturated solution of calcium in sodium at 712°, cannot be found accurately by cooling curves but a study of the 712°C. isotherm of the equilibrium reaction: $Ca + 2NaCl \rightleftharpoons 2Na + CaCl_2$ shows that point *a* corresponds to a solution containing 4 at.-% of calcium. Rinck's values differ considerably from those of Lorenz and Winzer who give the partial solubility limits as 0·8 and 86 at.-% of calcium and the temperature of the first horizontal as 700°C. On the branch *a*Na of the liquidus, Rinck confirms the existence of a eutectic approximating to pure sodium, it would appear that the weight of calcium dissolved in 100g. of sodium is 0·01g. at this eutectic. In Fig. 7 the area with respect to solid calcium is divided into two regions corresponding to two allotropic varieties of calcium. The heating curve of pure calcium shows a sharp change of internal energy at 450°C.; the alpha form of calcium is stable below 450°, the beta form between 450° and 848° the m.p. of calcium i.e. $Ca_\alpha \rightleftharpoons Ca_\beta - q$. For sodium-calcium alloys containing 90·55 to 35 at.-% calcium the transition temperatures are distributed between 394° and 446°C. respectively. The lowering of the transition temperature is due to lag phenomena and it is quite probable that the transition temperature is independent of the composition of the alloy.

At temperatures above 712°C. two liquid phases are present, saturated solution of calcium in sodium and saturated solution of sodium in calcium. In order to determine the composition of points, *b*, *b*′, *c*, *c*′, *d*, *d*′ marked on the solidification diagram in Fig. 7 Rinck has made use of the data obtained from the isotherms at 850°, 975° and 1100°C. for the reaction: $Ca + 2NaCl \rightleftharpoons 2Na + CaCl_2$. A slight extrapolation shows that the two metals are miscible in all proportions at temperatures above 1180°C.

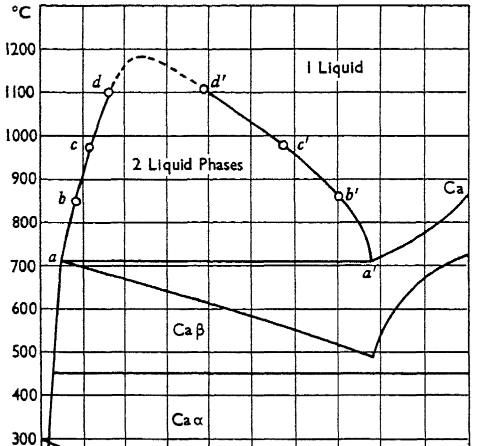

FIG. 7. EQUILIBRIUM DIAGRAM Na-Ca

According to Kroll[137] a calcium-sodium alloy containing 17% of sodium will stay in equilibrium with a salt bath containing 71% of calcium chloride at 850°C.: $CaCl_2 + 3Na \rightleftharpoons CaNa + 2NaCl$; by treating this alloy with large quantities of pure fused calcium chloride a nitrogen-free calcium may be obtained.

TABLE XVI. SOLIDIFICATION DIAGRAM OF CALCIUM-SODIUM ALLOYS

Wt. of Alloy g.	Ca At.-%	Na At.-%	Temp. of Commencing Crystallization °C.	Temp. of 1st. Horizontal (A) °C.	Time in Seconds of (A) 40 g.	Temp. of 2nd. Horizontal (B) °C.	Time in Seconds of (B) 40 g.
21·303	100	0	848	-	-	-	-
39·530	90·55	9·45	802	708	72	97·7	29
25·205	89·3	10·7	776	710	100	97·7	52
40·747	86·1	13·9	754	707	161	97·7	44
40·747	86·1	13·9	756	709	170	97·7	51
41·856	82·4	17·6	738	710	222	97·7	89
41·856	82·4	17·6	739	709	232	97·7	90
27·13	80·0	20·0	726	712	290	97·7	112
25·233	75·65	24·35	-	712	439	97·7	147
25·233	75·65	24·35	-	712	428	97·7	141
28·143	64·1	35·9	-	712	374	97·7	202
31·233	55·1	44·9	-	712	323	97·7	260
35·773	45·9	54·1	-	712	248	97·7	304
43·99	35·0	65·0	-	712	155	97·7	371
35·44	31·0	69·0	-	713	143	97·7	415
31·59	23·35	74·65	-	713	104	97·7	501
26·96	17·0	83·0	-	-	-	97·7	581
26·96	17·0	83·0	-	712	-	97·7	581
23·67	9·93	90·07	-	712	-	97·7	676
19·856	0	100	-	-	-	97·7	806

Calcium-sodium alloys containing 25–65% sodium can be separated by filtration[144] or vacuum distillation at elevated temperatures.[145] In the latter case sodium, sodium chloride and oxide-free calcium may be collected separately by using a heated condenser.

Calcium-sodium alloys containing 25–65% sodium, obtained as a by-product in the manufacture of sodium by the Downs process in which fused sodium chloride-calcium chloride is electrolyzed, may be used as a source of nitrogen-free calcium contaminated with only a few tenths of 1% of chloride and a few % of calcium oxide by treatment with ethyl alcohol.[137,146-148] The disposal of mixtures of metallic calcium and sodium by reaction with sodium hydroxide, is described by Padgett.[149]

The compositions of two bearing alloys containing calcium and sodium are roughly: (a) calcium 0·75–1·1; sodium 0·65–0·95; bismuth 0·10; antimony 0·25; magnesium 0·10; other metals 0·30% and the rest lead, (b) calcium 0·69; sodium 0·62; lithium 0·04, and lead 98·65%. The physical and mechanical properties such as hardness, corrosion resistance, limits of plastic flow, bonding strength with respect to the metal of the base, annealing temperatures are discussed. The abrasive resistance of these alloys compares favourably with that of a bearing alloy containing: tin 82, antimony 10·9, lead 3·1, copper 3·1%.[150]

Remy, Wolfrum and Haase[151] find that sodium is soluble in liquid strontium over the whole range of composition; it is not soluble in the solid state. No compound formation occurs but there is a eutectic at 92·5°C. and 3·2 at.-% of strontium.

Jellinek and Wolff[140] have studied the system: $Sr + 2NaCl \rightleftharpoons SrCl_2 + 2Na$ by electrolyzing the fused mixture in a fire-clay crucible with an antimony cathode. The equation to the curve obtained by plotting at.-% of metal as ordinate and mole % of its chloride as abscissa is: $x(1 - y)/(1 - x)y = K$. The equilibrium is not affected by temperature.

The solubility of barium in sodium is given by the expression: $\log W = 1{\cdot}2 - 0{\cdot}604 \times 10^3/T$ where W = wt.-% and T the temperature in °K. A solubility diagram is given below,[1] Fig. 8.

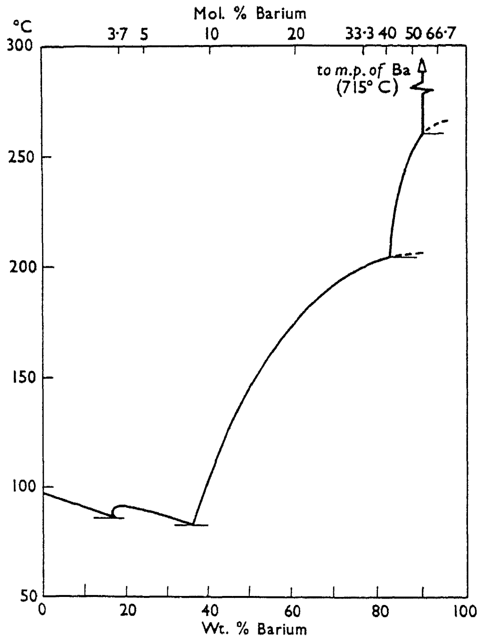

FIG. 8. BARIUM SOLUBILITY IN SODIUM

The phase diagram of the system, barium–sodium, has been prepared by Remy et al.,[151] c.f. Fig. 9. The equation does not appear to agree with the solubility diagram which is also different from Remy's phase diagram.

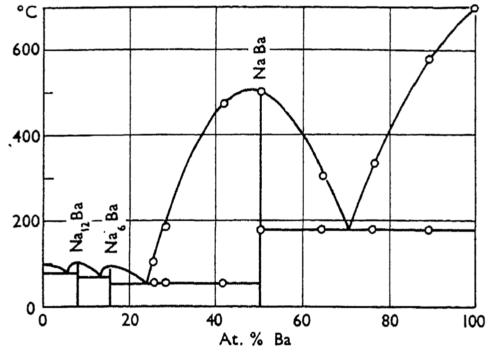

FIG. 9. EQUILIBRIUM DIAGRAM Na–Ba

Three compounds are shown, Na_2Ba, Na_6Ba and NaBa. There are also eutectics at 85°, 77°, 58° and 180° C.

The equilibrium $Ba + 2NaCl \rightleftharpoons BaCl_2 + 2Na$ has been studied by Jellinek and Wolff;[140] the fused mixture is electrolyzed in a fire-clay crucible with an electrode of tin, antimony or bismuth. The equation to the curve obtained by plotting at.-% of metal (ordinate) against mole % of chloride (abscissa) is: $x(1 - y)/(1 - x)y = k$. The equilibrium is quite independent of temperature, the cathode metal and even of the presence of water.

Zinc and sodium are only partially miscible;[1] at 557°C. zinc dissolves not more than 2·8% of sodium; when this alloy is solidified it consists of a zinc sodium compound in a zinc matrix.[137]

The electric potentials of sodium–zinc alloys have been measured by Kremann and Reiningshaus[152] who find that from 0–90% Zn the potential is practically the same as that of pure sodium. At 90% there is a drop of 1050 mV; from 92 to 98% of zinc the potential is practically constant at 400 mV. The authors assume the presence of a compound $NaZn_{12}$ in the sodium–zinc system, the potential of which is 1050 mV. "nobler" than sodium and 400 mV. less "noble" than zinc.

The reactions of sodium in liquid ammonia with solutions of zinc salts in the same solvent have already been described (see page 515). Kraus and Kurtz[153] and Burgess and Rose[154] found some indication of the presence of the compound $NaZn_4$; Zintl, Goubeau and Dullenkopf in their work on potentiometric titrations of sodium in liquid ammonia with liquid ammonia solutions of zinc iodide, obtained points of inflexion at compositions corresponding to $NaZn_{11\cdot8}$ and $NaZn_{12\cdot8}$ but were unable to confirm the presence of the compound $NaZn_4$.[129]

Zintl and Hauke[155,156] have since extracted a crystalline alloy of sodium and zinc with liquid ammonia and shown that it contains 2·6 wt.-% of sodium, i.e. it has the composition $NaZn_{13}$ and that it is a cubic compound with length of side a = 12·27A.; there are 112 atoms per unit cell and the alkali atom is surrounded by 24 equally distant zinc atoms. X-Ray, density and analytical data indicate unambiguously that the composition of the compound is $NaZn_{13}$. Powder diagram data are also given. Ketelaar[157] gives a = 12·25 A. for the side of the unit cell.

Sodium may be used to remove zinc after the desilverization of lead.[137] Ferrous metal such as sheet or wire may be coated with a zinc-sodium alloy containing up to 2% of sodium which serves to improve the quality of the coating.[158]

The phase diagram[125,126] is shown in Fig. 10.

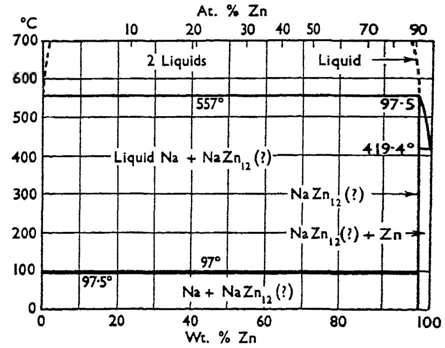

FIG. 10. EQUILIBRIUM DIAGRAM Na–Zn

The wetting of metallic zinc by liquid sodium has been investigated by Addison et al. by measuring contact angles over ranges of time and temperature. Electropolished zinc surfaces show a critical wetting temperature near 160°C.; chemical reaction between sodium and a zinc phosphate film deposited during electropolishing is considered to be responsible for this. No critical wetting temperature is observed for abraded zinc plates. The rates and mechanisms of wetting are discussed from the point of view of diffusion through surface films of zinc phosphate and zinc oxide and formation of the intermetallic compound $NaZn_{13}$. After removal of sodium by washing with water, microscopic examination of the surface indicates that the compound $NaZn_{13}$ reacts with water leaving behind zinc crystals without any major change in crystal form.[159]

Cadmium is miscible with sodium in all proportions. A simple eutectic is formed at 95·5°C. with 2·6% cadmium.[1]

Kremann and Reiningshaus[152] have measured the electric potential of cadmium–sodium alloys and found that from 0 to 66% of cadmium the potential is virtually that of pure sodium. At 66% the potential is decreased by 1300mV. and then remains constant to 80–85% when a further drop of 150 mV. is observed; the potential remains constant until 100% cadmium is reached. It is assumed from these results that the compounds $NaCd_2$ and $NaCd_5$ are responsible for the inflexions observed.

Kraus and Kurtz, by allowing cadmium iodide and cyanide in liquid ammonia to react with sodium in liquid ammonia, obtain rather inconclusive results for the ratio of sodium to cadmium in the reaction product, but conclude that the compound NaCd is probably formed.[153]

Zintl, Goubeau and Dullenkopf[129] (see also page 515) by potentiometric titrations of liquid ammonia solutions of cadmium iodide and sodium obtain results which appear to indicate that a compound of composition between Cd_5Na and Cd_7Na is formed under these conditions. The phase diagram given in Fig. 11[125,126] shows the presence of two intermetallic compounds $NaCd_2$ and $NaCd_6$. The crystal structure of the compound $NaCd_2$ has been investigated by Pauling[160] but the photographs are too complicated to assign indices with certainty to any of the spots. It may be that complex atom-groups are formed, as is the case in the formation of Pb_2 ions in a solution of sodium plumbide, $NaPb_2$, in liquid ammonia.

Kubaschewski and Catterall[38] critically review the thermochemical data obtained for the sodium–cadmium system by other workers and use some of the data to calculate the heat of formation, ΔH_{293} (g.-cal. per g. atom), latent heat of fusion (g.-cal. per g. atom), volume change on formation and partial free energies given in Tables XVII and XVIII.

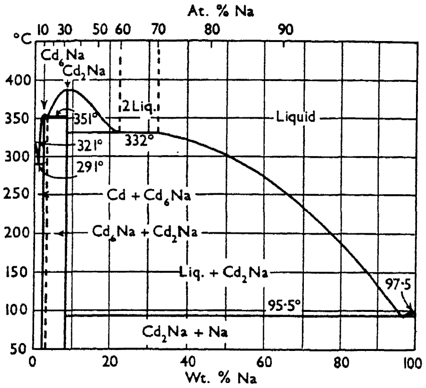

FIG. 11. EQUILIBRIUM DIAGRAM Na–Cd

TABLE XVII. THERMOCHEMICAL DATA FOR THE SODIUM-CADMIUM SYSTEM

	H_{293}	Lf	V_{298}
$\frac{1}{3}$ $NaCd_2$	−2800 ± 250	(1880)	−0·107
$\frac{1}{7}$ $NaCd_6$	−1800 ± 250	(1650)	−0·06

TABLE XVIII. PARTIAL FREE ENERGIES, SODIUM-CADMIUM SYSTEM

N_{Na}	$\Delta\bar{G}_{Na}$(668°K.)
0·15	−4150
0·20	−2660
0·3	−1450
0·4	−770
0·50	−430
0·60	−250
0·80	−175

The heats of fusion estimated from the duration of arrests on cooling curves are probably not accurate and are given in brackets. Possible values for the integral free energy for the composition $NaCd_2$, i.e. ΔG_{668}, for the heat of formation, $\Delta H_{liq.}$ and the integral entropy of solution, $\Delta S_{liq.}$ are −1480, −2150 g.-cal. per g. atom and −1·0 g.-cal. per degree/per g. atom respectively. For the intermetallic compound $NaCd_6$, $\Delta S_{liq.} = -0{\cdot}4$. There is some uncertainty in evaluating these properties so they should not be regarded as absolute values.

The solubility of cadmium in sodium is given by the expression $W = -16{\cdot}8 + 0{\cdot}203t$ where W = wt.-% and t = °C.[1]

The reaction between air and a jet of sodium solution in another metal is usually vigorous at high temperatures, accompanied by a flame, dense smoke of the reaction products and, where the sodium content is high, a mild explosion. Sodium-cadmium alloy containing 0·1 mole fraction of sodium tested at 700°C. in dry air at atmospheric pressure gives a vigorous reaction.[132]

Jänecke[118] has examined the system sodium-cadmium-mercury and has shown that the compounds $NaCd_2$, m.p. 385°, and $NaCd_4$, m.p. probably 360°, are present in the system. For the reaction: $2NaCdHg \rightarrow NaCd_2 + NaHg_2$, Halla has calculated the free energy of formation as 910 g.-cal./mole at 300°C.[119] The activity of sodium in liquid alloys, Na-Cd-Hg, of various compositions at 300°–400°C. has been derived from e.m.f. measurements; wide departure from ideal behaviour is found. The activity of mercury in the same system has been calculated from vapour pressure data and again wide departure from ideality is obtained.[151]

The data of Frauenschill and Hall[161] obtained at 400° C. have been used by Kubaschewski and Catterall[38] to calculate the partial free energies $\Delta\bar{G}_{Na}$ (liq.) and $\Delta\bar{G}_{Hg}$ (liq.). The integral free energies of mixing: N_{Na} (liq.) + N_{Hg} (liq.) + N_{Cd} (liq.) to form the liquid alloy i.e. ΔG_{673}, have also been calculated and are given in Table XIX. The energy values refer to g.-cal. per g. atom.

TABLE XIX. FREE ENERGY DATA FOR THE Na-Cd-Hg SYSTEM (400°C.)

$\Delta\bar{G}_{Na}$	N_{Na}	N_{Hg}	$\Delta\bar{G}_{Hg}$	N_{Hg}	N_{Cd}	ΔG_{673}	N_{Na}	N_{Hg}
-2000	0·368	0·126	-1000	0·68	0·256	-2180	0·1	0·72
-2000	0·484	0·258	-1000	0·75	0·125	-3800	0·3	0·56
-2000	0·576	0·339	-1000	0·792	0·042	-3560	0·6	0·32
-4000	0·23	0·154	-2000	0·53	0·376	-1170	0·9	0·08
-4000	0·334	0·333	-2000	0·618	0·191	-2280	0·1	0·60
-4000	0·436	0·451	-2000	0·698	0·060	-3610	0·3	0·47
-6000	0·148	0·17	-3000	0·404	0·477	-3150	0·6	0·27
-6000	0·23	0·385	-3000	0·522	0·239	-1000	0·9	0·07
-6000	0·346	0·523	-3000	0·618	0·074	-2290	0·1	0·45
-8000	0·154	0·423	-4000	0·294	0·565	-3330	0·3	0·35
-8000	0·278	0·578	-4000	0·448	0·276	-2740	0·6	0·20
-	-	-	-4000	0·542	0·092	-885	0·9	0·05
-	-	-	-5000	0·21	0·632	-2020	0·1	0·30
-	-	-	-5000	0·39	0·305	-2770	0·3	0·23
-	-	-	-5000	0·488	0·103	-2270	0·6	0·13
-	-	-	-	-	-	-730	0·9	0·03
-	-	-	-	-	-	-1630	0·1	0·18
-	-	-	-	-	-	-2180	0·3	0·14
-	-	-	-	-	-	-1700	0·6	0·08
-	-	-	-	-	-	-500	0·9	0·02

The compounds of sodium with mercury, their appearance and melting points have already been referred to (see page 440).

In his account of new methods and results on the detection of intermetallic compounds, Grube[162] refers to the melting points of the alkali mercurides and to their phase diagrams. The light alkali metals form compounds less rich in mercury than do the heavier ones, the limits ranging from Li_6Hg to $CsHg_{10}$; the alkali mercuric compounds containing the greatest amount of alkali metal are Li_6Hg, Na_3Hg, KHg. The m.p. of comparable alkali mercury compounds decrease with rising atomic number of the alkali metal. The compounds appear to be metals but are similar in their chemical properties to salts. They show a positive temperature coefficient of electrical conductivity and by "transport" work show a wandering of the ions. When the compounds are formed by melting the components together, the reaction is of a vigorously explosive type and much heat of reaction is produced.

Zviagincev[163] has suggested a method by means of which the composition of intermetallic compounds may be determined from the ionization potentials. If the ionization potential of metal A is denoted by J_A, i.e. the energy required to sever the ion from the atom, and the atomic volume by V_A, then the ratio J_A/V_A i.e. the atomic concentration of the ionization energy, will be different for different metals, and if metal B dissolves in metal A there will be places created in the crystalline lattice of the alloy where $J_A/V_A >$ or $< J_B/V_B$. This restrains the movement of electrons whereby the electrical conductivity is reduced. Solid solutions are always less conducting than pure metals.

Intermetallic compounds are characterized by maxima on composition–

electrical conductivity curves, and the author supposes that at these points, since the motion of electrons is not so strongly restrained as in solid solutions, the energy concentrations of the two metals are probably equal i.e. $J_A/V_A = J_B/V_B$. If n = at.-% of A and $100 - n$ = at.-% of B then $J_A/nV_A = J_B/(100 - n)V_B$ or $n = J_AV_B \times 100/J_BV_A + J_AV_B$ at.-%. The number of intermetallic compounds calculated in this way will probably be higher than those which can exist, and those compounds belonging to unstable or scarcely probable ions, and those failing to satisfy the requirements of crystal chemistry e.g. compositions in which the number of atoms of one component very greatly exceeds the number of atoms of the other, should be rejected. In the system sodium-mercury, where the ionization potentials are 10·39, 29, 65 for mercury and 5·116, 52 for sodium and the atomic values are 14·1 and 23·7 respectively; the computed compounds are as shown in Table XX.

TABLE XX. COMPUTED INTERMETALLIC COMPOUNDS OF SODIUM-MERCURY

Computed		Observed	
At.-% Hg	Formula	At.-% Hg	Formula
9	$HgNa_9$	–	–
25	$HgNa_3$	25	$HgNa_3$*
48·4	HgNa	50	HgNa
69	Hg_2Na	67·8	Hg_2Na
77·5	$Hg_{3(4)}Na$	80	Hg_4Na
96	$Hg_{24}Na$	–	–

* Actually given as $HgNa_8$

The computed values of $HgNa_9$ and $Hg_{24}Na$ are rejected.

Sodium and mercury form the following intermetallic compounds: Na_3Hg, Na_5Hg_2, Na_3Hg_2, NaHg, Na_7Hg_8, $NaHg_2$, $NaHg_4$, (see phase diagram Fig. 12).[125] A eutectic point lies at 60·5% Hg and 21·5°C., and down to this point the solubility of mercury in sodium may be represented by: $\log(1 - W/100) = 1{\cdot}5642 - 579{\cdot}85/T$ where W = wt.-% and T is expressed as °K.[1] In the liquid state there is complete miscibility.

The heats of formation of solid sodium amalgams have been determined by Biltz and Meyer,[164] Kubaschewski and Seith[165] and Kawakami.[35]

The values obtained have been critically reviewed by Kubaschewski and Catterall.[38] In view of the variety of methods used there is generally good agreement; the results of Biltz and Meyer do not deviate by more than 0·5 kg.-cal. from the selected values given in Table XXI the data in which are based on the earlier work of Berthelot[166] and Kubaschewski and Seith. At concentrations of $N_{Na} < 0{\cdot}333$, the results of Kawakami agree satisfactorily but at concentrations >0·4 his results are about 1·3 kg.-cal. more negative.

The free energies of formation shown in Table XXI have been derived by Kubaschewski and Catterall from e.m.f. measurements made by Bent and Forziate.[167] Entropies of formation also given have been obtained from the above free energies and heats of formation. The negative values of ΔS refer to the formation of solid alloys from solid sodium and liquid mercury; if the entropy of fusion of mercury is introduced, the entropies of formation of $NaHg_2$ and Na_3Hg_2 are slightly negative, and those of the other compounds positive between 0·25 and 0·75.

Volume changes on alloy formation, ΔV_T, where $\Delta V = (V \text{ alloy} - \Sigma V \text{ metals})/\Sigma V$ metals at temperature T, are also given in Table XXI and these values have been taken from Vanstone[168] and Biltz.[169]

ΔS_T is expressed as g.-cal./degree/g.-atom.

The data given by Kubaschewski and Catterall[38] in Table XXII for liquid amalgams has been obtained from the following sources.

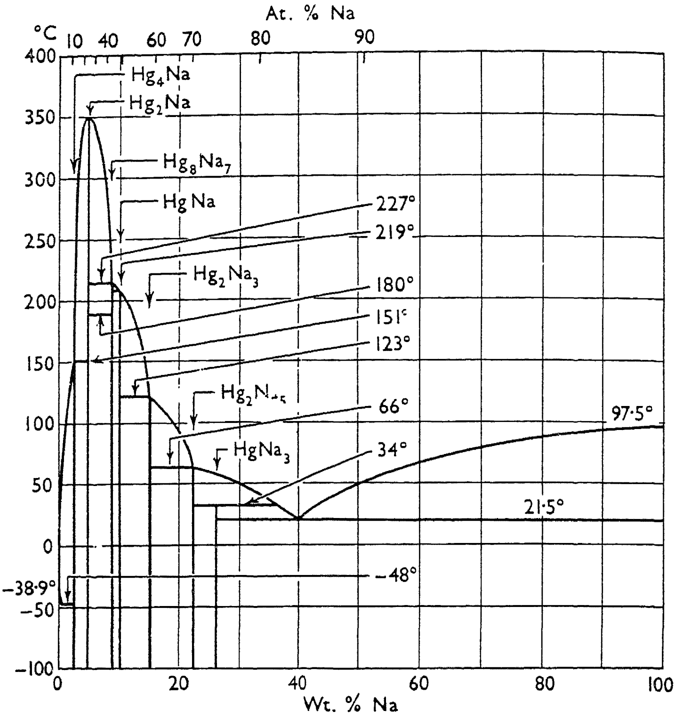

FIG. 12. EQUILIBRIUM DIAGRAM Na-Hg

TABLE XXI. HEATS OF FORMATION OF SOLID SODIUM AMALGAMS

Compound	ΔH_{298} g.-cal./g.-atom	ΔG_{298} g.-cal./g.-atom	ΔS_{298} g.-cal./deg./g.at.	ΔV_{298}
$\frac{1}{5}$ $NaHg_4$	−4000 ± 200	−3660	−1·14	−0·14
$\frac{1}{3}$ $NaHg_2$	−6000 ± 250	−5500	−1·68	−0·19
$\frac{1}{15}$ Na_7Hg_8	−5300 ± 250	−5160	−0·47	−0·21
$\frac{1}{2}$ NaHg	−5150 ± 250	−4940	−0·70	−0·205
$\frac{1}{5}$ Na_3Hg_2	−4600 ± 200	−4210	−1·27	−0·16
$\frac{1}{7}$ Na_5Hg_2	−3300 ± 250	—	—	—
$\frac{1}{4}$ Na_3Hg	−2900 ± 300	−2800	−0·15	−0·15

Measurements of e.m.f. have been made by Shibata and Oda[170] for amalgams containing up to 5 at.-% of sodium. The partial free energies $\Delta\overline{G}_{\text{Na}}$ (solid) (25°C.) are based on these results and a single determination by Lewis and Kraus[171] for an amalgam containing $N_{\text{Na}} = 0{\cdot}0175$ at room temperature. The values of $\Delta\overline{G}_{\text{Na}}$ (liq.) (375°C.) have been derived from the work of Hauffe[172] who has measured the e.m.f. of sodium-sodium amalgam cells for $N_{\text{Na}} = 0{\cdot}45$ - 0·93, with sodium-glass as electrolyte at 299°C. and 375°C. The partial free energies $\Delta\overline{G}_{\text{Hg}}$ (liq.) (335°C.) have been derived from the work of Bent and Hildebrand[173] who have measured the pressure of mercury over amalgams containing up to 48 at.-% of sodium at 335° and 375°C. Both $\Delta\overline{G}_{\text{Na}}$ and $\Delta\overline{G}_{\text{Hg}}$ are expressed in calories.

Since e.m.f. data obtained by Hauffe and Bent and Hildebrand refer to two temperatures only, the temperature coefficient and hence the partial heats of solution cannot be assumed to be accurate. In order to combine the partial heats obtained at room temperature with those obtained at higher temperatures it has been assumed that ΔC_p is zero because of lack of data to the contrary. In Table XXII $\Delta\bar{H}_{\mathrm{Na}}$ (liq.) (g.-cal.) values for N_{Na} less than 0·06 have been derived from the results of Shibata and Oda (25°C.) and those for $N_{\mathrm{Na}} > 0{\cdot}4$ from Hauffe (299–375°C.). Kawakami's results for the integral heats of mixing for liquid amalgams, where $N_{\mathrm{Na}} < 0{\cdot}14$ at 110°C., have been used together with a value obtained by Roos,[174] from the heat of formation of solid $NaHg_2$ and from its heat of fusion ($Lf = 2060$) determined by the duration of arrest-points on cooling curves, and with the $\Delta\bar{H}_{\mathrm{Hg}}$ values to derive $\Delta\bar{H}_{\mathrm{Na}}$ for $N_{\mathrm{Na}} =$ 0·1 - 0·4. It is considered that the heat data given in Table XXII should be checked experimentally.

TABLE XXII. THERMODYNAMIC DATA FOR LIQUID Na-Hg SYSTEMS

N_{Na}	$\Delta\bar{H}_{\mathrm{Na}}$ liq.	$\Delta\bar{H}_{\mathrm{Hg}}$ liq.	$\Delta\bar{G}_{\mathrm{Na}}$ solid 25°C.	$\Delta\bar{G}_{\mathrm{Na}}$ liq. 375°C.	$\Delta\bar{G}_{\mathrm{Hg}}$ liq. 335°C.	ΔH liq.	ΔV_{298}
0·001	-20,580	-	-21,550	-	-	-	-
0·01	-20,500	-	-20,000	-	-	-	-0·004
0·05	-20,000	(-90)	-18,280	-	-100	-1,090	-0·030
0·1	(-18,700)	(-220)	-	-	-300	-2,070	-0·062
0·2	(-13,500)	(-770)	-	(-11,400)	-980	-3,350	-0·114
0·3	(-8,800)	(-1,840)	-	-7,950	-2,070	-3,950	(-0·165)
0·4	-5,250	(-3,400)	-	-5,000	-3,630	-4,170	-
0·5	-2,250	-	-	-2,940	-5,800	-4,070	-0·186
0·6	-800	-	-	-1,590	-	-3,600	-0·171
0·7	-70	-	-	-830	-	-2,850	-0·147
0·8	+180	-	-	-410	-	-1,850	-0·102
0·9	+130	-	-	-150	-	-900	-0·057

Values in parentheses are liable to error

Volume changes on formation of liquid amalgams have been determined by Vanstone[168] and appear to be independent of temperature.

The preparation of sodium amalgams has been described by several authors. Amounts up to 15 kg. have been obtained by melting sodium under toluene in a steel vessel fitted with a loose lid carrying a thermocouple pocket, which can also be used as a stirrer, and a lead through which mercury is slowly added. During the early stages there may be bursts of flame or even slight explosions but these do not lift the lid; the latter portion of mercury may be added more rapidly. The whole apparatus must be well ventilated with a hood to carry away mercury vapour which may escape from the vessel. When the amalgam is completely melted it is stirred and poured into a round-bottomed kettle to cool.[175] A detailed study of the formation of sodium amalgam by electrolysis of sodium chloride solutions has been made by Tesh and Woodward[176] using various types of platinum electrodes. The most satisfactory results are obtained with unplatinized platinum electrodes. The effect of current density, voltage, temperature, and concentration of the electrolyte have been studied. In the formation of sodium amalgam from sodium salts by electrolysis the flat metal bottom parallel to the diaphragm and anode is inclined to the horizontal at about 1:10 and mercury flows over it. This arrangement permits the loading of the cell with a higher current density and gives the most economic yield over its whole area.[177] An apparatus for carrying out the electrolytic preparation of sodium amalgam and for its continuous reaction in a chemical process is described by de Nora.[178]

Flake sodium amalgam containing 2·75% of sodium is first obtained in the form of fine flocculi by pouring hot liquid amalgam into a jar of xylene or kerosene agitated by an electric stirrer, allowing it to settle and then drying in an air current.[179] Solidified tablets of sodium amalgam containing 23% of sodium for use as electrodes in galvanic cells are prepared and handled under oil. The hot amalgam is poured into holes in a steel plate or in an endless strip of metal and cooled in oil.[180]

An account of the electrical properties of sodium amalgams known up to 1925 is given by Schulze.[181]

Concentration changes due to the passage of an electric current through sodium amalgams have been investigated by several workers.[182-187] Electrolysis of liquid amalgams is carried out in tubes of fine bore, and composition changes along the length of the tubes determined.

For amalgams containing up to 2·1 wt.-% Na, the anode becomes enriched with sodium; for amalgams of higher sodium content, the cathode becomes enriched. Numerous tables and graphs are given.

For amalgams containing 32–35·5 wt.-% Na the electrolytic effect i.e. the difference between the percentage of sodium at the anode and cathode ends of the capillary, first increases with length of the capillary and then reaches a constant value; the effect also increases with time and then remains unaltered. The greater the content of sodium in the amalgam the greater is the electrolytic effect, and the greater the cross sectional area of the capillary the smaller the effect. The transference numbers of sodium towards the anode first increase, then decrease, pass the zero at 2·1% of sodium, then change their sign and steadily increase.[187]

Drakin[188] has stated that when an electric current is passed through a metallic phase for a short time (i.e. before the back diffusion becomes noticeable) the "transference number" $mF/It = Dc(V_1 - V_2)F_2p/RT$ where F is the faraday, m the number of g.-atoms transferred in time t by the current I; D is the diffusion coefficient, c the concentration, p the electrical resistivity and V_1, V_2 the average charges of "solvent" and "solute" ions respectively, i.e. the number of free electrons originating from a component of the alloy divided by the total number of the atoms of this component. In the system Hg–Na, $V_1 - V_2$ is 0·0286. In the steady state the concentrations at the anode, C_a, and cathode C_c should satisfy the equation $\ln(C_a/C_c) = E/T$ where E is the potential difference between the electrodes and T the absolute temperature. This equation is confirmed by the data of LeBlanc and Jäckh.[184]

When amalgams are formed by a discharge of sodium ions at a mercury cathode in a glass vessel, a wedge of electrolyte penetrates between the amalgam and the glass at a minimum potential. This is considered to be due to a very strong adsorption of discharged metal ions at the interface. The forces holding the wedge in equilibrium seem to be largely electro-osmotic.[189]

The electrical conductivities of sodium amalgams have been determined by a number of workers.[190-194] The results given in Table XXIII have been obtained at 30°C. by a potentiometric method.[193]

TABLE XXIII. ELECTRICAL CONDUCTIVITY OF SODIUM AMALGAM AT 30°C.

Wt.-% Na in Amalgam	Resistivity of Amalgam $\times 10^{-6}$	Specific Conductivity $\times 10^{4}$
0·0183	97·38	1·0269
0·0314	97·70	1·0235
0·0524	98·33	1·0176
0·0702	98·86	1·0115
0·0790	96·20	1·0395
0·1068	96·90	1·0330
0·1226	97·34	1·0273
0·1313	97·70	1·0235
0·1696	98·54	1·0148
0·1776	98·83	1·0118
0·2026	99·49	1·0051
0·2254	100·10	0·9990
0·2364	100·70	0·9930
0·2680	101·50	0·9852
0·2714	95·48	1·0473
0·2899	96·99	1·0310
0·2987	97·68	1·0237
0·3174	98·40	1·0102

Resistivity of Mercury $\times 10^{-6}$ = 96·69
Conductivity of Mercury $\times 10^{4}$ = 1·0342

The electrical conductivity decreases with an increase in the concentration of sodium until it reaches a minimum value at 0·07% Na where a discontinuity occurs. A second discontinuity is observed at 0·268% Na. These breaks in the conductivity-concentration curve may correspond to complexes of sodium with mercury. The same values for the electrical conductivity of sodium amalgam at 30°C. are obtained whether the measurements are made by direct or alternating current. These results support the view that conduction in amalgams is not electrolytic, in which case a higher value of the conductivity, due to polarization effects, should have been obtained by the alternating current method. The conductivities of the amalgams have been calculated according to the mixture law and in all cases it has been found that the calculated results are higher than the observed values. Sodium amalgams do not therefore appear to be mechanical mixtures of sodium and mercury.[193]

Davies and Evans[194] have measured the conductivities of eleven amalgams containing 0·307 to 5·270 at.-% sodium at eight temperatures from 0–300°C. The relative resistance for a constant concentration up to 3·6% increases with temperature up to 185°C. At constant temperature the resistance rises to a maximum with increasing concentration and then falls. The resistance of the amalgams is greater than that of mercury except at 5·27 at.-% where a solid mass which appears to have a crystalline structure separates out.

The viscosity of a sodium amalgam was found by Paranjpe[195] to decrease gradually with time but the original value could be obtained again by subjecting the amalgam to agitation; the effect was thus not due to the instability of the amalgam. Degenkolbe and Sauerwald[196] have measured the viscosity of sodium amalgams over the whole concentration range from 360–400°C. A marked maximum is obtained in the viscosity-concentration isotherm in the concentration region of the most stable compound, Na_2Hg.

Liquid sodium amalgams are abnormal in that the thermal conductivity increases with temperature and at a more rapid rate as the sodium content increases.[197] The thermal conductivity of liquid sodium decreases in a normal manner as the temperature increases. Alloys containing 70–94 at.-% sodium have been examined over the temperature range 100–150° C.; from the straight lines obtained when the thermal conductivities are plotted against temperature, the values found at 100° and 150° C. are as shown in Table XXIV.

TABLE XXIV. THERMAL CONDUCTIVITIES OF SODIUM AMALGAMS AT 100° C. AND 150° C.

At.-% Na	Thermal Conductivity Watt/cm. - °C.	
	100° C.	150° C.
70	0·0887	0·1029
71·4	0·0907	0·1031
73·1	0·0903	0·1039
73·8	0·0916	0·1052
75·1	0·0921	0·1063
76·1	0·0934	0·1076
77·6	0·0960	0·1105
79·1	0·0983	0·1121
80·0	0·0996	0·1141
80·4	0·1022	0·1169
82·1	0·1073	0·1219
83·9	0·1146	0·1303
86·4	0·1266	0·1437
86·9	0·1362	0·1532
88·4	0·1463	0·1662
90·6	0·1619	0·1827
93·7	0·2140	0·2456

Curves of thermal conductivity at 100° C. plotted against concentration show breaks at 71·4 and 75·0 at.-% Na, probably caused by the presence of the intermetallic compounds Na_5Hg_2 and Na_3Hg, and another at 86·5 at.-% Na which would agree with the eutectic found by Vanstone[168] at 85·5 at.-% Na.

The vapour pressures of eight amalgams, ranging in concentration from 1:1 to 15:1 mol. ratio of mercury to sodium have been measured over a maximum temperature range of −56° C. to 90° C. and the results are typified by the selected data given in Table XXV.

TABLE XXV. VAPOUR PRESSURES OF SODIUM-MERCURY AMALGAMS

Concentration of Amalgam	Temp. °C.	Vapour Pressure mm. Hg
Hg : Na = 0·985:1	44·6	$2{\cdot}90 \times 10^{-7}$
	57·1	$8{\cdot}12 \times 10^{-7}$
	72·2	$2{\cdot}97 \times 10^{-6}$
	90·8	$1{\cdot}32 \times 10^{-5}$
Hg : Na = 1·19:1	46·3	$2{\cdot}66 \times 10^{-7}$
	56·4	$9{\cdot}46 \times 10^{-7}$
	72·0	$4{\cdot}73 \times 10^{-6}$
	84·3	$1{\cdot}82 \times 10^{-5}$
Hg : Na = 1·63:1	9·58	$8{\cdot}08 \times 10^{-8}$
	21·39	$3{\cdot}96 \times 10^{-7}$
	31·08	$1{\cdot}38 \times 10^{-6}$

continued on following page

TABLE XXV (continued)

Concentration of Amalgam	Temp. °C.	Vapour Pressure mm. Hg
	40·85	$3{\cdot}45 \times 10^{-6}$
	59·75	$1{\cdot}36 \times 10^{-5}$
Hg : Na = 1·96:1	−14·17	$5{\cdot}01 \times 10^{-7}$
	−6·02	$7{\cdot}96 \times 10^{-7}$
	−0·08	$1{\cdot}69 \times 10^{-6}$
	+6·07	$2{\cdot}86 \times 10^{-6}$
	14·37	$8{\cdot}58 \times 10^{-6}$
	28·63	$5{\cdot}98 \times 10^{-5}$
	40·64	$2{\cdot}57 \times 10^{-4}$
	51·80	$9{\cdot}91 \times 10^{-4}$
Hg : Na = 3·41:1	−8·83	$1{\cdot}02 \times 10^{-5}$
	4·38	$2{\cdot}38 \times 10^{-5}$
	23·68	$2{\cdot}13 \times 10^{-4}$
	35·74	$6{\cdot}48 \times 10^{-4}$
Hg : Na = 5·86:1	−47·68	$3{\cdot}25 \times 10^{-7}$
	−19·26	$9{\cdot}02 \times 10^{-6}$
	−1·71	$8{\cdot}58 \times 10^{-5}$
	14·15	$7{\cdot}69 \times 10^{-4}$
Hg: Na = 5·78:1	−49·77	$1{\cdot}72 \times 10^{-7}$
	−22·64	$8{\cdot}22 \times 10^{-6}$
	−0·51	$8{\cdot}86 \times 10^{-5}$
	9·20	$4{\cdot}57 \times 10^{-4}$
	16·98	$9{\cdot}53 \times 10^{-4}$
Hg : Na = 15·71:1	−56·68	$2{\cdot}99 \times 10^{-8}$
	−26·55	$3{\cdot}69 \times 10^{-6}$
	−10·48	$3{\cdot}35 \times 10^{-5}$
	−0·04	$9{\cdot}36 \times 10^{-5}$
	2·62	$1{\cdot}36 \times 10^{-4}$
	9·41	$4{\cdot}62 \times 10^{-4}$
	18·26	$1{\cdot}01 \times 10^{-3}$

The log p *vs* $1/T$ graphs are approximately straight lines. The van't Hoff isochore has been used to calculate the internal energy charge: $\ln p_2/T_2 - \ln p_1/T_1 = U/\mathbf{R}(1/T_1 - 1/T_2)$, where p_1 and p_2 are the saturated mercury vapour pressures of the amalgams, T_1 and T_2 the respective temperatures on the absolute scale, $\mathbf{R}$ the gas constant and U the total change of internal energy when a gram molecule of the amalgam is formed, i.e. U is the heat of reaction at constant volume. The heats are considered to be accurate to within say ±200 g.-cal. and are found to vary from 15,000g.-cal. for amalgams rich in mercury to 14,000g.-cal. for the 2:1 amalgam. The greater part of the heat is liberated in the formation of the compounds, Na_3Hg, Na_2Hg, etc. and it follows that the heat of dilution is comparatively small. Gerke[198] has calculated the free energy change for a 5:1 Hg:Na amalgam to be 18,300g.-cal. from electrochemical data, i.e. it is about 3,000g.-cal. greater than the internal energy change as calculated from the log p *vs* $1/T$ graphs. This is in agreement with the work of Richards and Conant[199] on the temperature gradient of concentration cells of sodium amalgams; the temperature gradient of the e.m.f. is positive and comparatively large giving a considerable difference between the free and internal energy change.

The vapour pressure of 1:1 sodium amalgam has been extrapolated to 20°C. and found to be 3×10^{-8} mm. The time required for sufficient mercury to diffuse through 100 cm. of tubing of 1 cm. internal diameter to form a 1:1 amalgam with 10g. of sodium is found to be 1554 days. This means that a sodium mercury vapour trap containing 10g. of sodium should hold the mercury vapour beyond the tube down to 10^{-8} mm. for 1500 days under the cited conditions.[200]

Bent and Hildebrand[173] have measured the vapour pressures of sodium amalgams from 281° to 378°C. and calculated the activity of mercury from p/p_0, values. The data given in Table XXVI may be represented by the equation: $\log a_1/N_1 = KN_2^2/T$ where a_1 = activity of mercury, and N_1, N_2 mole fractions of mercury and sodium respectively.

TABLE XXVI. ACTIVITY OF MERCURY IN SODIUM AMALGAMS

Temp. °K.	N_1 Mole Fraction Hg	Activity of Hg (a_1) p/p_0
572·9	0·774	0·343
608·5	0·961	0·941
608·5	0·939	0·894
608·5	0·872	0·692
608·5	0·773	0·348
608·5	0·740	0·272
608·5	0·541	0·016
608·5	0·529	0·021
608·5	0·511	0·011
648·1	0·872	0·701
648·1	0·627	0·080
648·1	0·611	0·066

The relative partial molar heat content of mercury given in Table XXVII is calculated from the temperature coefficient of the amalgams referred to pure mercury as the standard state. This gives the free energy of transfer of mercury in amalgams.

TABLE XXVII. RELATIVE PARTIAL MOLAR HEAT CONTENT OF MERCURY IN SODIUM AMALGAM

N_2 Mole Fraction of Na	Relative Partial Molar Heat Content	
	Observed	Calculated
0·128	−76	−81
0·226	−204	−225
0·373	−665	−694
0·389	−765	−752

The activity of sodium is calculated from the known activity of mercury by the integration of the Duheim equation or graphically:-

$$\ln a_2/N_2 = -\int \frac{N_1}{N_2} d\ln a_1/N_1$$

and for a given value of N_2 the e.m.f. of a cell in which the reaction is the transfer of sodium to amalgam is given by the equation: $E = RT\ln a_2/23074$. If N_2 = 0·01772 the e.m.f. of such a cell is 1·07V. at 648·1°K. and 1·03V. at 608·5°K. By extrapolation to 25°C. the e.m.f. is found to be 0·88V. which is in agreement with the value of 0·85V. obtained by Lewis and Kraus.[171]

The deviation from Raoult's Law is expressed by β in the equation: $\log a_1/N_1 = \beta N_2{}^2$ and at 25°C. $\beta = -20{\cdot}0 \pm 0{\cdot}4$ for sodium amalgam. A similar value is obtained for potassium amalgam at 307°C. and caesium amalgam at 497°C. The deviations from a perfect solution shown by sodium amalgam can be explained on the assumption that compounds are formed.

Bent and Swift[201] have measured the e.m.f. of dilute amalgams with concentration cells containing sodium iodide in dimethylamine. The results at 5°, 15° and 25°C. have been used to calculate the temperature coefficients, -dE/dT, given in Table XXVIII.

TABLE XXVIII. TEMPERATURE COEFFICIENT dE/dT FOR DILUTE SODIUM AMALGAMS

NNa	Temp. °C.	-dE/dT
0·043955	5	0·000059
0·04870	15	0·000043
0·05380	25	0·000029
-	10 – 35	0·000032

Deviations from Raoult's Law attributed to the formation of compounds soluble in mercury are not borne out by the experimental results with very dilute solutions.

Vapour pressure abnormalities have been observed in capillary-active amalgams containing 2·6 at.-% of sodium at 12°C. Measurements of the absorption of resonant light, 2537A., show a vapour pressure lowering of 55% from 6·45 × 10^{-4} mm. for pure mercury to (2·9 ± 0·3) × 10^{-4} mm. for the above amalgam. Agitation of the amalgam causes the vapour pressure to rise to that of pure mercury which indicates that in a static system alkali metal is adsorbed on the mercury surface and that the photosensitivity of amalgams is due to this.[202]

Sodium amalgams containing the following ratios of sodium to mercury: 1:100, 1:500, 1:2000, 1:5000 and 1:10,000 have been distilled at 26 - 1 mm. Hg at 300°C. and the loss of sodium from the still after 98% of the mercury has been distilled never exceeds 0·1mg. per 200g. of amalgam.[203] From the measured heat of formation of the compound Na_3Hg and by application of Nernst's heat theorem, Wartenberg[204] has found that there appears to be a considerable proportion of the compound in the vapour above the amalgam at 444°C. The accuracy of this deduction has been queried by Eucken and Neumann[205] who have shown that Na_3Hg must be dissociated in the vapour state by distillation at constant pressure. According to Barratt[206] the absorption spectra of the vapours of the alkali amalgams show well defined bands which confirm the presence of compounds in the vapour state but give no information as to their compositions; Pedder and Barratt[207] state that sodium amalgam having the composition of Na_3Hg and distilled at 444°C. gives a distillate the composition of which shows that the amalgam distils over unchanged.

In order to extract sodium from amalgams containing less than 10% by weight of sodium the amalgam is distilled to remove mercury until the concentration of sodium reaches 10% when it is treated with a solvent which dissolves the alkali metal but not the mercury; sodium is recovered from the solvent.[208, 209]

The relative densities of alkali-metal amalgams have been described by Bain and Withrow.[210] Oily or partly liquid amalgams are due to fine crystals in the liquid. Bhatnagar et al.[211] have measured the densities of sodium amalgam relative to benzene using a specific gravity bottle; the densities with respect to water given in Table XXIX have then been calculated from the density of benzene.

TABLE XXIX. DENSITIES OF SODIUM AMALGAMS

Wt.-% Na	Density
0·000	13·52
0·033	13·49
0·053	13·47
0·072	13·46

continued on following page

TABLE XXIX (continued)

Wt.-% Na	Density
0·084	13·45
0·143	13·40
0·172	13·38
0·207	13·35
0·238	13·31
0·266	13·29
0·299	13·27
0·302	13·26
0·312	13·25

The interfacial tension between liquid amalgams and pure benzene has been measured by means of a modified dropping pipette kept at 30°C. By counting the number of drops in a given volume of liquid *A* issuing from a pipette with an orifice of known diameter and counting those of a reference liquid *B* the ratio $T_A/T_B = n_B d_A/n_A d_B$ where T_A, n_A, d_A are respectively the surface tension, number of drops and density of liquid *A* and T_B, n_B, d_B the corresponding quantities for liquid *B*. The values of the interfacial tension of the liquid amalgam given in Table XXX have been calculated from the above values by assuming the interfacial tension of mercury-benzene is 100 dynes per cm.

TABLE XXX. INTERFACIAL TENSION OF SODIUM AMALGAM AT 30°C

Wt.-% Na	I.T. dynes/cm.
0·000	100
0·033	99
0·053	98
0·072	124
0·084	119
0·143	106
0·172	100
0·207	92
0·238	88
0·266	87
0·299	106
0·302	103
0·312	92

There is a marked deviation from the mixture law which suggests that compounds of sodium and mercury are formed even at very low concentrations of the alkali metal. At all other concentrations the amalgam is probably a solution of the compounds and the metal in mercury.[211]

Oppenheimer[212] found that the surface tension of mercury is reduced by small additions of alkali metals, as shown in Table XXXI.

TABLE XXXI. RELATIVE SURFACE TENSION OF SODIUM AMALGAMS AT 20°C

Wt.-% Na	Relative Surface Tension dynes/cm.
0·000	437
0·025	399
0·019	404
0·021	402

Bradley[213] found that for dilute amalgams, $d\sigma/d(\log a_2)$, where σ = surface tension and a_2 is the activity of the dissolved metal, is constant. Values of the surface excess are in agreement with compound formation in the surface layer, roughly to the extent of $NaHg_6$.

Sauerwald *et al.*[214] give the values of 257 and 307 dynes/cm. for the surface tension of the alloy $NaHg_2$ at 270° and 390°C. respectively.

The surface tensions of amalgams reported by Semenchenko *et al.*[215,216] and given in Table XXXII at first decrease with concentration of the alkali metal and then remain constant.

TABLE XXXII. SURFACE TENSION OF SODIUM AMALGAMS (Semenchenko *et al.*)

Concentration	Surface Tension dynes/cm.	Reference
0·000	410	215
0·0045 at.-% Na	386	215
0·135 at.-% Na	337	215
0·00305 g.-at./l.	386	216
0·00537	368	216
0·0130	356	216
0·0167	354	216
0·0332	348	216
0·0369	337	216
0·0523	328	216
0·0911	337	216

Pugachevich[217] has investigated the effect of temperature on the surface tension of alkali metal amalgams. For pure mercury and amalgams containing up to about 0·6 wt.-% of sodium the fall of surface tension, σ, is non-linear, the curve being slightly concave to the temperature axis. Both sodium and potassium are surface-active; for sodium the limiting surface activity is about three times its activity at 350°C.

Surface tensions of amalgams containing 8×10^{-5} to 0·284 at.-% of sodium have been measured at 22°C. in a vacuum. Even at the lowest concentration, 8×10^{-5} at.-% Na, a decrease of 2–3 dynes/cm. in the surface tension of mercury occurs.[218]

The relatively small paramagnetism exhibited by sodium amalgams is considered by Franke and Katz[219] to be due to the fact that sodium is not predominantly present in the form of atoms but essentially in the same state as in concentrated solutions of sodium in liquid ammonia. The specific susceptibilities of amalgams containing 21–95 wt.-% of sodium have been measured and the atomic susceptibilities of sodium calculated from Wiedemann's law of mixtures on the assumption that the susceptibility of mercury remains constant. The susceptibility/concentration curve passes through a maximum at about 90% sodium. The atomic susceptibility remains almost constant at 15×10^{-6} between 21 and 90% of sodium; in this region thermal analysis shows the presence of Na_3Hg and Na_5Hg. The accuracy of the magnetic measurements at lower concentrations of sodium is insufficient to permit definite conclusions to be reached.

Heat transfer coefficients for dilute solutions of sodium in mercury, containing 0·0018–0·0063% of sodium, from room temperature to about 160°F. in forced convection, have been determined by Doody and Younger.[220]

The nature of sodium amalgams, i.e. whether they are colloidal or true solutions, has been the subject of much controversy. According to Paranjpe and Joshi[221] sodium amalgams containing up to 0·14% sodium are colloidal in nature with sodium as the disperse phase, mercury as the dispersing medium and Na_xHg_y as the colloidal micelles with varying values for x and y. Such solutions do not undergo sedimentation on standing. These authors also consider that the properties of the amalgams depend on the method of preparation as well as on the colloidal nature of the solutions. Bent[222] on the other hand finds no evidence that sodium amalgams are colloidal and cites freezing point data and photomicrographs to indicate that the amalgams are true solutions. The f.p. depression of mercury in dilute amalgams is 1·9°C. per at.-% by calculation from Raoult's law and the experimental value is also 1·9°C. For more concentrated amalgams a larger depression is observed whereas a colloidal solution would give a smaller depression. Also the vapour pressure lowering for dilute amalgams is that calculated for an ideal solution and in more concentrated amalgams the lowering is greater than for an ideal solution whereas a smaller value would be obtained for a colloidal solution. Joshi[223] considers however that the probability that a colloidal system is present is greater than Bent admits. From his work on thermal conductivities of sodium amalgam Hall[197] states that it is evident that these data afford no evidence in favour of the colloidal nature of sodium amalgams and that breaks in the thermal conductivity/composition curves occur either at compounds or a eutectic and at no other point. Also there is good agreement between the measurements of Boohariwalla[193] and Davies and Evans[194] on the electrical conductance of sodium amalgams, both finding a discontinuity at 0·272% Na although admittedly the former author also finds a second one at 0·079%. The variation of the reducing properties of sodium amalgam mentioned by Paranjpe and Joshi is probably due to the presence of impurities. More recently the structure of sodium amalgam of sodium content less than 2·5% has been studied by Inoue and his co-workers[224-227] and Nakamura *et al.*[228] Hexagonal prismatic or needle-like crystals of $NaHg_5$, $NaHg_6$, $NaHg_7$, $NaHg_8$, $NaHg_9$, $NaHg_{10}$, $NaHg_{11}$, and $NaHg_{14}$ have been obtained by Inoue[224] by cooling melted amalgam or by electrolyzing a saturated solution of sodium chloride with a mercury cathode. The sodium–mercury diagram at atmospheric pressure has been obtained. The crystals are unstable if subjected to pressure, which may be due to a small free-energy change. The amalgam is considered to be composed of various crystals as well as liquid solution. It is suggested that the crystals obtained by electrolysis are composed of $NaHg_4$ and mercury bonded weakly by their charges. The structure of sodium amalgam is considered as a sort of colloidal state.[225] In a later communication Inoue *et al.* have studied the structure of sodium amalgam with regard to the experimental results of deamalgamation potential, equilibrium potential, electrophoresis, surface tension, viscosity and thixotropy and consider that the electric charge of the amalgam plays an important role in the formation of sodium amalgam which they say is in the colloidal state.[226] In the solid state, amalgams containing 1·26% or more of sodium are charged negatively. In the liquid state singular points are observed at concentrations of 0·16, 0·23 and 0·38% Na. The authors conclude that sodium amalgam appears to be in two-phase equilibrium. The time taken for crystals to appear on the mercury surface when a saturated solution of sodium chloride is electrolyzed at a current density greater than 20amp./sq. dm. is similar for that required for hydrogen to be evolved. At lower current densities it takes longer for the evolution of hydrogen.[228]

Supersaturation occurs as shown by experiments without stirring. The crystals separating out in the above experiments are in the form of fine needles. The presence of vanadium, aluminium and magnesium ions promotes crystal formation.[228] The concentration distribution of sodium in mercury in the case of amalgamation and deamalgamation is due to the diffusion of sodium–mercury into mercury and the difference of surface tension between sodium and mercury. The distribution is only irregular at the beginning of the electrolysis when the cluster of sodium-mercury crystals is formed on the surface of the cathode.[227]

The reaction of sodium amalgam with water, aqueous alkali and acid solutions in the presence and absence of sodium chloride, with and without the addition of foreign materials, has been studied by many workers. This work, and methods used for denuding sodium amalgam, have been discussed elsewhere.[229]

Many references occur in the literature to the evolution of hydrogen on treatment of sodium amalgam with water; distilled and pure water have been used and the sodium amalgam made by mixing the metals together and by electrolysis of sodium carbonate or sodium chloride. Sodium amalgam prepared from the metals by mixing in iron crucibles is decomposed by water 30–50 times faster than electrolytic sodium amalgam.[230]

Bhatnagar *et al.*[231] report that sodium amalgam reacts with water in the dark at a rate which can be measured by the volume of hydrogen evolved. Klein[232,233] working with large amounts of amalgam (50ml.) containing 0·5 wt.-% of sodium, so that the composition of the amalgam should remain reasonably constant during tests, quotes average rates of reaction at 25°C. on treatment with 200 ml. of distilled water: in the first 6 min. the volume of hydrogen evolved is 2·1 ml./min., after 1 hr., 1 ml./min., after 2 hr., 0·8 ml./min. and after 3 hr., when the strength of the sodium hydroxide solution formed is 0·08N., 0·6 ml./min. Bhatnagar finds that amalgams containing 0·081, 0·158, 0·214, 0·311 wt.-%of sodium react with water at 25°C. on exposure to light from a carbon arc, in such a way that there is a steady increase in the initial rate of reaction with concentration of sodium in the amalgam, the difference between the rates over the dark reaction approaching something like constancy after the first 30 min. Fraenkel, Wengel and Cahn[234] find that after the constant velocity period, *i.e.* when the sodium concentration has fallen to the order of 0·5–1 milliequivalents per 100g. of mercury, the reaction appears to be unimolecular; he gives the unimolecular constants of 146, 110, 116 for three experiments, carried out at 30°C. with stirring at 450r.p.m. Anand and Bhatnagar[235] working with amalgams prepared electrolytically have examined the effect of polarized light on the action with water and found that this is greatest when the electric vector vibration is parallel to the incident plane and least when it is at right angles to it.

Miller and Riedel[236] attribute the outstanding catalytic action of various metals, such as the ferrous alloys of molybdenum, vanadium, tungsten and chromium, on the velocity of decomposition of sodium amalgams by water to a surface increase.

Klein[232] has shown that the rate of decomposition of sodium amalgam with 1·0N. sodium chloride solution is much lower than with distilled water.

The results given in Table XXXIII refer to solutions of different normalities of sodium ion produced from sodium chloride initially added and from sodium hydroxide formed, equivalent ot the amount of hydrogen liberated, during the reaction. The volume of aqueous phase in experiments 1 and 2 is 200 ml. and in 3 it is 300 ml.

TABLE XXXIII. RATE OF REACTION OF SODIUM AMALGAM WITH SODIUM CHLORIDE SOLUTIONS AT 20°C.

	Normality of Na ion	Period of Time min.	Rate of Reaction ml. H_2 at N.T.P. per min.
1	0·02	30	0·518
	0·05	20	0·478
	0·11	20	0·448
	0·21	21	0·412
	0·41	20	0·364
	0·88	25	0·344
	1·70	20	0·328

continued on following page

TABLE XXXIII (continued)

	Normality of Na ion	Period of Time min.	Rate of Reaction ml. H_2 at N.T.P. per min.
2	0·02	12	0·457
	0·07	10	0·436
	0·27	12	0·399
	0·57	24	0·360
	1·06	30	0·331
	2·04	40	0·310
1	0·03	15	0·841
	0·09	15	0·665
	0·15	16	0·566
	0·27	24	0·460
	0·50	53	0·376
	1·16	28	0·329

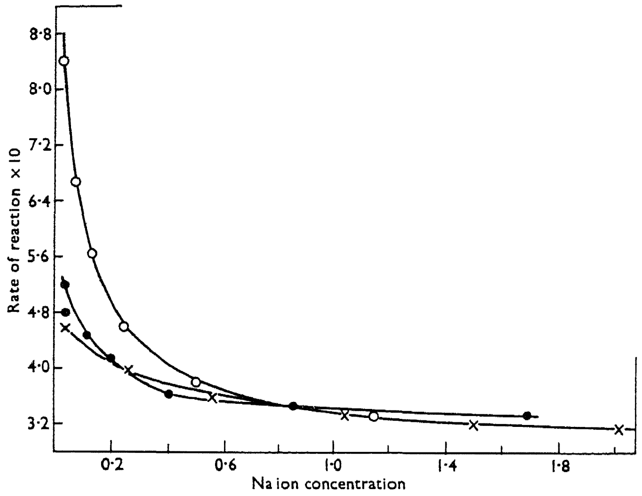

FIG. 13. RATE OF REACTION OF SODIUM AMALGAM WITH NaCl SOLUTIONS

As may be seen from Fig. 13, where the rate of reaction is plotted against the sodium ion concentration, the rate decreases as the sodium ion concentration increases; the rate of reaction is the greater the smaller is the sodium chloride concentration and the rate of reaction decreases more rapidly the greater is the original rate of reaction. Reproductibility of results in solutions of the same concentration of sodium chloride is not good.

TABLE XXXIV. EFFECT OF RATE OF STIRRING OF SODIUM AMALGAM WITH 200 ml. 2N.NaCl SOLUTION AT 25°C.

Rate of Stirring r.p.m.	Period of Time min.	Rate of Reaction ml. H_2 at N.T.P./min.
0	10	0·350
113	6	0·360
203	9	0·370
500	10	0·370
500	10	0·360

The rate of reaction as shown in Table XXXIV is apparently independent of the rate of stirring. A temperature coefficient of 1·44 per 10°C. has been obtained from the series of experiments recorded in Table XXXV.

TABLE XXXV. EFFECT OF TEMPERATURE ON THE RATE OF REACTION OF SODIUM AMALGAM WITH 1·0N. NaCl SOLUTION

Temp. °C.	Period of Time min.	Rate of Reaction ml. H_2 at N.T.P./min.
15	20	0·260
15	28	0·250
25	17	0·375
35	14	0·530

Another series of experiments carried out at 20°–50°C. gives a temperature coefficient of 1·46 per 10°C.

Volkov[237] has determined the effect of adding various compounds to sodium amalgam on the rate of decomposition in brine: the amounts added are given in brackets as mg./l. followed by the volume of hydrogen in ml. liberated in 30 min. $CuSO_4$ (100, 0·4); nitrates of: Ag (10, 0·15), Be (1000, 0·2), Th (10, 0·3), U (1·0, 0·2); chlorides of: Mg (10, 0·1), Ca (10, 0·1), Sr (100, 0·1), Ta (10, 0·2), Ba (10, 0·1), Zn (100, 0·1), Cd (10, 0·1), Y (10, 0·2), La (10, 0·6), Ce (1000, 0·3), Pr (1000, 0·4), Nd (1000, 0·3), Sm (1000, 0·4), Eu (1000, 0·2), Er (1000, 0·3), Ti (10, 0·15), Zr (10, 0·15), Sn (1000, 1·3), Pb (1·0, 0·05), Bi (10, 0·1), Mn (1·0, 0·05), Fe (1·0, 0·3), Co (10, 0·1), Ni (1·0, 0·4), Ru (0·1, 0·2), Rh (0·1, 0·2), Pa (0·01, 0·1), NH_3 (100, 0·7), $NaVO_3$ (0·01, 4·5); sodium arsenite (10, 0·1); sodium antimonate (100, 0·6), Na_2CrO_4 (0·1, 2·5), Na_2MoO_4 (0·1, 1·2), $NaWO_4$ (10, 0·1), $NaTeO_4$ (10, 0·45), K_2OsCl_6 (0·1, 0·2), K_2PtCl_6 (0·01, 2·2), alk. soln. of Ge (0·01, 0·2), tantalic acid fused with $NaHCO_3$ (1000, 0·1), NH_4Ga alum (100, 0·1), borax (1000, 0·3), $AlCl_3$ (1·0, 0·2), $KReO_4$ (0·1, 0·15). The maximum rate of decomposition without the additions is that obtained by Iofa *et al.*[238]

It has also been shown that in the absence of other impurities, the negative ions, SO_4^{--}, Br^-, I^-, F^-, and ClO_3^- in concentrations up to 0·1g./l. have no effect on the decomposition rate of sodium amalgam by shaking with buffered solutions of sodium chloride. Certain substances, e.g. silicates, borates, pyrophosphates and stannates deactivate vanadium which has been shown to promote the decomposition rate to a very high degree.[239]

Reproducible results are not obtained for the amount of hydrogen liberated in unit time when sodium amalgam is acted on by alkaline solutions.[232,233,240] The reaction is catalyzed by reduced iron, vanadium, tungsten, nickel, manganese, and by alloys of vanadium, tungsten, silicon, molybdenum, titanium, zirconium, and boron, as well as by salts of vanadium and tungsten. Cast iron has only a feeble action.[241]

The decomposition of sodium amalgam containing 0·1–0·3% of sodium with caustic soda at 20°C. has been studied by Morgenstein[242] in the presence and absence of other metals. For the measurement of potential a graphite electrode was employed. The electrode was "poisoned" by impurities (lead, copper, tin or zinc) in the amalgam. Contact resistance between graphite and amalgam was, however, reduced by iron and the results given in Table XXXVI show the rate at which hydrogen was liberated from sodium amalgam under the conditions stated.

In other experiments graphite was immersed in ferric chloride solution and then heated to dull redness, when iron oxide was formed on the surface and in the pores. This material and untreated graphite when used for the decomposition of sodium amalgam containing 0·1% sodium with 50% sodium hydroxide

TABLE XXXVI. DECOMPOSITION OF 0·25% SODIUM AMALGAM WITH NaOH SOLUTIONS

Temp. °C.	ml. Hydrogen/min.			
	5% NaOH		50% NaOH	
	Contact with Fe	No Contact	Contact with Fe	No Contact
20	17·03	0·49	3·29	0·18
50	25·80	1·45	9·84	0·58
75	28·80	2·20	15·53	1·01
90	29·30	2·90	–	–
100	–	–	16·26	1·18

solution gave the results recorded in Table XXXVII.

TABLE XXXVII. DECOMPOSITION OF SODIUM AMALGAM IN THE PRESENCE OF GRAPHITE

Temp. °C.	ml. H_2/min. Untreated Graphite	ml. H_2/min.				
		Graphite Immersed in $FeCl_3$ Solution and Heated				
		Once	Twice	Thrice	Four Times	Five Times
22	0·6	1·5	1·8	2·2	2·5	2·8
50	1·9	9·9	10·9	11·8	12·7	12·9
105	4·5	31·9	31·7	31·7	31·9	31·9

The rate of decomposition of sodium amalgam in alkaline solution has been examined by Volkov[243] who placed an amalgam containing 0·055% of sodium in a saturated sodium chloride solution leaving it to stand for eleven days but removing daily all the spots which gassed strongly and all visible surface layers. The lowest rate of solution at pH 12 was found to be $1{\cdot}4 \times 10^{-4}$ ml. H_2/sq.cm.hr. which corresponds to hydrogen overvoltage of 1·8V. at a current density of 1 amp. This overvoltage is greater than previously believed.

Trümpler and Gut[244,245] have studied the kinetics of sodium amalgam decomposition. The rates of decomposition in aqueous solutions of borate buffers, pH 8·2 – 9·2 at 25°C. determined by measuring the volume of hydrogen liberated, are unchanged by making the amalgam the cathode in an electrolysis cell with current densities up to about 25ma./sq.cm. The lower rates of reaction thus found, as compared with the results of others, are believed to be due to the absence of impurities which catalyze the decomposition. The rates are expressed by the following equation where $iD(H_2)$ is the current density and N_2 is mole fraction of Na in the amalgam:- $iDH_2 = N_2^{0{\cdot}5} \times 10^{-2{\cdot}53} + 7{\cdot}80N_2 + 3{\cdot}76N_2^2$. Impurities are shown to increase the rate of hydrogen evolution. The effect of rate of stirring is due to the increase in amalgam surface in contact with the electrolyte solution.

Volkov and Klitsa[246] have measured current densities in cells having a 0·1% sodium amalgam anode, a graphite cathode and aqueous solutions of sodium hydroxide. It was calculated that about 25% of the graphite surface took no part in the reaction. Kapstan and Iofa[247] have studied the decomposition of amalgams and hydrogen overvoltage on mercury in alkaline solutions.

The rates of reaction of sodium amalgam with dilute hydrochloric acid in the presence of sodium chloride have been measured by Klein.[232] Results obtained at 2 or 3 min. intervals over a period of about 3·5 hr., during which time the solution, at first acid, becomes neutral and finally alkaline, are typified by a few given in Table XXXVIII, the whole range of results being shown however in Fig. 14.

TABLE XXXVIII. RATES OF REACTION OF SODIUM AMALGAM WITH DILUTE HYDROCHLORIC ACID

Time min.	Vol. of H_2 liberated ml.	C	C'	Rate of Reaction (v) ml. H_2/min.	$Q = \frac{v - k}{C'}$
0	2·60	174·80	-	-	-
2	6·75	170·65	172·70	2·075	0·0102
4	10·85	166·55	168·60	2·050	0·0102
7	16·85	160·55	163·55	2·000	0·0102
9	20·75	156·65	158·60	1·950	0·0102
11	24·55	152·85	154·75	1·900	0·0101

(Volume of sodium chloride solution: 200 ml. 0·5 N., Temperature 25°C., Surface of Contact, 6 sq.cm., Rate of Stirring, 340 r.p.m. The volume of hydrogen liberated is corrected to atmospheric pressure.) C is the volume in ml. of hydrogen which would be liberated by the acid from a given moment to the moment when it is all neutralized; C' is the average value of two consecutive C values, and is proportional to the concentration of unconsumed acid in solution at a stated time.

The rate of reaction has been plotted against C' in Fig. 14. Lines B and C refer to two other experiments in which the following conditions exist, B: 100ml. 0·5N. sodium chloride solution, Surface of Contact 9sq.cm., Rate of Stirring, 262r.p.m.; C: 300ml. of the same strength solution as B, Surface of Contact 18sq.cm., Rate of Stirring, 243r.p.m. Both B and C have been carried out at 25°C.

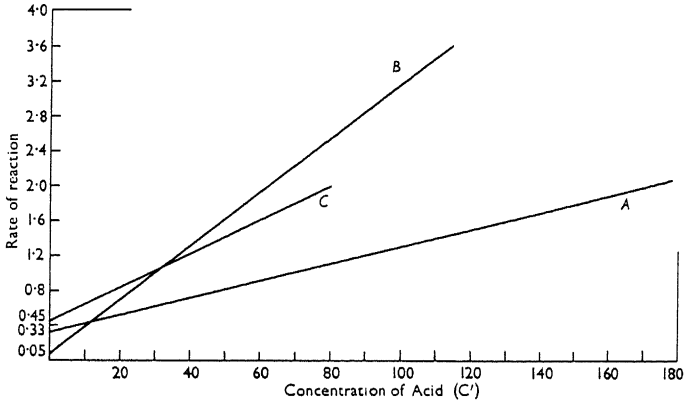

FIG. 14. RATES OF REACTION OF SODIUM AMALGAM WITH DILUTE HYDROCHLORIC ACID

These three experiments have been carried out in the presence of excess of sodium. After the acid has been neutralized, the reaction proceeds at a constant rate in alkaline solution.

As may be seen from Fig. 14 the rate of reaction in acid solution decreases with acid consumption. The ordinate at $C' = 0$ is the constant value obtained in neutral or slightly alkaline solution and the equation of the lines, A, B and C, (rate of reaction) = $QC' + k = V$ is used to calculate Q. By integrating the expression $-dC/dt = KC + k$, within the limits C_1 and C_2 and $t_1 - t_2$, the following equation is obtained:-

$$K = \frac{2{\cdot}303}{t_2 - t_1} \log \frac{C_1 + {}^{k}/K}{C_2 + {}^{k}/K}$$

The rate of reaction in acid solution is thus composed of two factors, one which represents the rate in neutral or weakly alkaline solution, and the other which is at every moment proportional to the acid concentration. Under given conditions the proportionality factor, K, is reproducible but k varies from experiment to experiment. K is also independent of the concentration of the amalgam, but is dependent on the rate of stirring.

The temperature coefficient is about 1·07 per 10° C.

The relation between the rate of stirring and rate of reaction of liquid sodium amalgam with dilute hydrochloric acid has been examined in greater detail by Klein.[248]

In Fig. 15 the rates of reaction have been plotted against rate of stirring for three series of experiments and the straight lines so obtained extrapolated to zero rate of stirring to obtain the value, a. The values for n, rate of stirring, K, rate of reaction, and the expression $\frac{K-a}{n}$ are given in Table XXXIX.

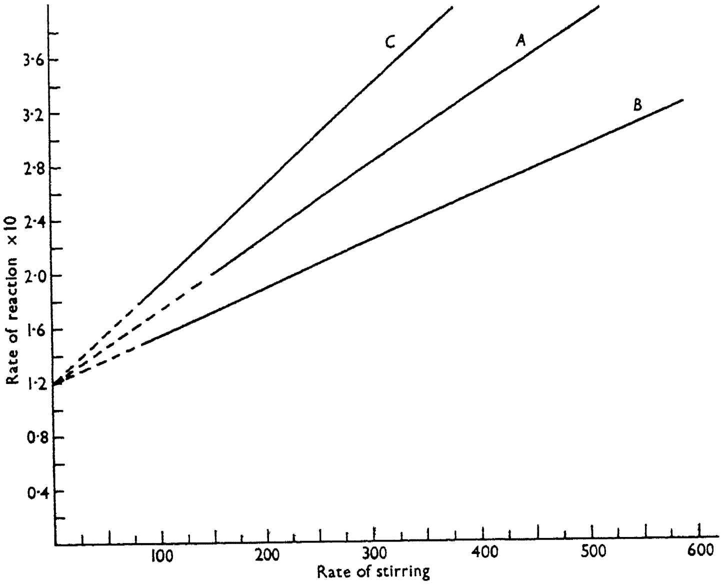

FIG. 15. RATE OF REACTION OF SODIUM AMALGAM WITH DILUTE HYDROCHLORIC ACID

TABLE XXXIX. REACTION BETWEEN LIQUID SODIUM AMALGAM AND DILUTE HYDROCHLORIC ACID AT 25°C.

(a)	n	121	185	324	363	444		a = 0·120
	K	0·186	0·225	0·292	0·310	0·365		
	$\frac{K-a}{n}\cdot10^3$	0·541	0·568	0·531	0·523	0·552		
(b)	n	83	139	255	290	429	545	a = 0·120
	K	0·149	0·169	0·212	0·220	0·270	0·312	
	$\frac{K-a}{n}\cdot10^3$	0·351	0·350	0·359	0·346	0·349	0·352	
(c)	n	88	214	261	273	343		
	K	0·193	0·282	0·320	0·325	0·358		
	$\frac{K-a}{n}\cdot10^3$	0·775	0·733	0·747	0·734	0·680		a = 0·125

These results show that in a heterogeneous system such as this the rate of reaction is made up of two factors, one constant for a given reaction and the other proportional to the rate of stirring. The proportionality factor is dependent on the stirring device and is indeed distinctly influenced by slight alterations.

Sodium amalgam, containing a maximum of 0·46 wt.-% of sodium and prepared by electrolyzing sodium chloride solutions with a mercury cathode, has been treated with dilute hydrochloric acid in the presence of sodium chloride and the rate of evolution of hydrogen (volume measured at atmospheric pressure) and the electric potential of the amalgam against a calomel electrode determined during the course of the reaction.

In the example detailed in Table XL, sodium amalgam of cross sectional area, 4·10sq.cm. is stirred at 450r.p.m. at 25°C. with 600ml. of 0·1N. hydrochloric acid containing 4g. of sodium chloride. The amount of acid used is about 15 times in excess of that required.

TABLE XL. DECOMPOSITION OF SODIUM AMALGAM WITH 0·1N. HCl AND NaCl

Time min.	Volume of H_2 v (ml.)	$\Delta v/\Delta t$	Potential (Scale Divisions)
0	0	-	107·8
0·5	5·2	10·4	107·5
1	10·3	10·2	107·5
2	20·2	9·9	107·8
3	29·7	9·5	108·0
4	39·7	10·0	107·8
5	49·6	9·9	107·5
6	59·8	10·2	107·0
7	69·5	9·7	105·0
8	77·9	8·4	83·0
8·5	79·3	2·8	80·0
9	79·8	1·0	77·5
10	80·4	0·6	73·5
11	80·6	0·2	72·0
12	80·7	0·1	70·0
16	81·4	-	65·0
33	82·2	-	7·5
80	82·3	-	0

There is no induction period, and as may be seen from Fig. 16 the reaction proceeds at a constant rate, averaging 9·9ml. H_2/min., until just before the end when the rate falls practically to zero as the last traces of sodium dissolve.

The potential of the amalgam remains steady at 107·5 scale divisions or -2·06 volts (measured against a calomel electrode) until the rate of gas evolution decreases and then it drops suddenly and then more gradually and finally more quickly again until it reaches the null-point. The existence of well-defined compounds of sodium and mercury, which are weakly dissociated, is considered to account for the initial constant rate of reaction.

The presence of a small amount of impurity such as copper causes the initial and final potentials to be higher, but the rate of evolution of hydrogen remains the same.

The effect of temperature on the rate of reaction has also been measured, as shown in Table XLI, the temperature coefficient for a 10° rise being 1·24.

The initial constant rates of reaction, ml. H_2/min., the electric potentials and diffusion coefficients of lithium, sodium and potassium amalgams are compared in Table XLII.

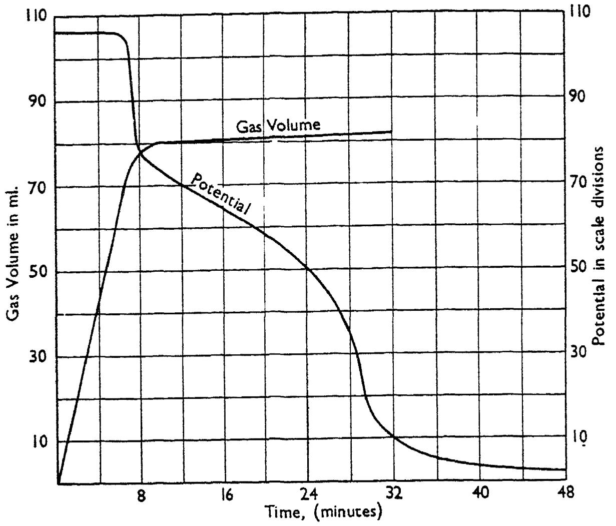

FIG. 16. DECOMPOSITION OF SODIUM AMALGAM WITH 0·1N. HCl AND NaCl

TABLE XLI. EFFECT OF TEMPERATURE ON THE DECOMPOSITION OF SODIUM AMALGAM WITH 0·1N. HCl + NaCl

Temp. °C.	Initial Constant Rate of Reaction ml. H_2/min.	Average Rate of Reaction ml. H_2/min.
15	7·4 - 8·6	8
15	7·4 - 8·6	8
25	9·7 - 10·2	9·9
25	10	
25	9·5 - 10·1	

Initial Potential (Scale Readings)	Total Vol. H_2 Liberated ml.
80	101·8
80·2	103·3
107·5	82·3
107·5	69·3
111	34

TABLE XLII. COMPARISON OF Li-, Na-, K- AMALGAMS

Properties	Lithium Amalgam	Potassium Amalgam	Sodium Amalgam
Initial Constant Rate of reaction (ml. H_2/min.)	9·0	9·5	9·9
Initial Potential against the Normal Calomel Electrode (volt)	-2·33	-2·18	-2·06
Normal Potential against the Normal Calomel Electrode (volt)	Li = -3·3	K = -3·20	Na = -2·99
Diffusion Coefficient (found)	$7{\cdot}63 \times 10^{-6}$	$6{\cdot}02 \times 10^{-6}$	$7{\cdot}41 \times 10^{-6}$
cm.^{2}/sec. (calculated)	$7{\cdot}34 \times 10^{-6}$	$4{\cdot}80 \times 10^{-6}$	$5{\cdot}91 \times 10^{-6}$

There is no agreement between the diffusion coefficients of the metals in mercury and the initial rates of reaction; lithium, according to the diffusion coefficient, should dissolve more quickly than potassium, but the difference in their rates of reaction is only slight. Also, the rate of evolution of hydrogen for the different amalgams does not change in the same way as the electromotive force.[249]

Fraenkel, Wengel and Cahn,[234] using a similar technique, find that after the constant velocity period the reaction is unimolecular. They have also measured the effect of acid concentration on the decomposition of sodium amalgam with the results shown in Table XLIII.

TABLE XLIII. EFFECT OF ACID CONCENTRATION ON DECOMPOSITION OF SODIUM AMALGAM AT 30°C.

Acid Concentration	Initial Constant Velocity ml. H_2/min.	Volume of Amalgam Used (about 0·5 wt.-% Na) ml.
0·05N. HCl	5·4	7·35
0·1N. HCl	10·6	6·5
0·2N. HCl	21·0	7·6

Brönsted and Kane[240] in 1931 critically reviewed earlier work and consider the evidence in favour of a unimolecular reaction to be unconvincing. They used an amalgam of 0·024M. initial concentration (21 c.c.) and a pH not lower than 7·5 because with more acid solutions the reaction proceeds too quickly to permit accurate measurements. In all cases the temperature was 18°C., and the reaction velocity was determined by following the pressure of hydrogen evolved. As observed by earlier workers, the reaction suddenly comes to a stop. Pressure–time curves are not those of a unimolecular reaction nor is the sudden cessation of reaction compatible with unimolecular reactions. An approximately linear relation is found to exist between the velocity of reaction and the square root of the concentration of sodium in the amalgam: $kt = 2(\sqrt{a} - \sqrt{x})$ where a and x are the initial and final sodium concentrations and k the velocity constant, which depends on the dimensions of the apparatus. The linear relation between time and concentration holds for all solutions examined except sodium hydroxide solution. Whereas a unimolecular reaction requires an infinite time for completion, the reaction described above for the dissolution of sodium amalgam is completed in a finite time. In the equation: $kt = 2(\sqrt{a} - \sqrt{x})$, if $x = 0$ and $t = t_\infty$ then:-

$$t_\infty = \frac{2\sqrt{a}}{k}$$

i.e. the reaction time is finite. In aqueous solutions of disodium hydrogen phosphate, glycocoll and phenol buffers, the rate varies directly with the concentration of the acid molecule. The rate of reaction with phenol in dry benzene is directly proportional to the phenol concentration. The results agree with the proposed mechanism of a reaction between metal (electron) and acid molecules. The roseo-cobaltic ion, which carries three positive charges, reacts very rapidly with sodium amalgam and this is attributed to the resulting strong attraction to the metal electron. The dissolution of sodium in strong acids is considered to be governed by the rate of a diffusion process.

Amalgams containing >0·05% of sodium wet iron of low carbon content; there is no tendency for iron dissolution into mercury.[250]

Numerous references occur in the literature to the deamalgation of sodium amalgam on a commercial scale.[229,251-275]

The industrial use of sodium amalgam as a reducing agent in alkaline as well as acid media is discussed by Poma and Pellegrini.[276]

Metals in finely powdered form may be obtained from solutions of their salts e.g. antimony from its compound, Na_3SbS_3, by injecting these solutions through a column of sodium amalgam containing 0·2–0·5% sodium.[277]

The separation of cadmium and lead from their solutions by the addition of sodium amalgam is described by Kozlovskii *et al.*[278]

Magnesium amalgam is prepared by treating sodium amalgam with magnesium compounds, such as the oxide or halides or mixtures of compounds, in an inert non-aqueous solvent such as aniline or pyridine. Organic nitrogen-containing bases are the best solvents.[279]

The solubility of aluminium in sodium has been determined by Scheuer,[280] Fink, Willey and Stumpf[281] and by Ransley and Neufeld.[282]

Individual measurements made by Scheuer[280] by quenching the metal contained in a closed iron crucible and protected with a hydrogen atmosphere showed a wide deviation; average solubility values in aluminium containing 0·1% of silicon and 0·2% of iron were: >0·1% Na at 700°C., 0·11% at 750° and 0·13% at 800°C.

Fink *et al.*[281] have examined the equilibrium relations in aluminium–sodium alloys of high purity containing from 0–0·2% sodium. At a pressure of 1 atm. and at 659·0°C. a monotectic occurs between aluminium-rich liquid solution containing 0·18 wt.-% of sodium, sodium-rich liquid solution and aluminium solid solution. The solubility of sodium in liquid aluminium decreases at higher temperatures and is 0·155% at 800°C. The solubility of sodium in solid aluminium is reported as less than 0·003% at temperatures approaching the monotectic.

The solid solubility of sodium in aluminium has been measured directly by Ransley and Neufeld.[282] In high-purity aluminium the solubility at 650°–550° is approximately 0·002%; the temperature coefficient appears to be very small. The monotectic composition is given as 0·14% of sodium and the solubility is found to increase smoothly to 0·25% at 775°C. The phase diagram for Na–Al[125] is shown in Fig. 17.

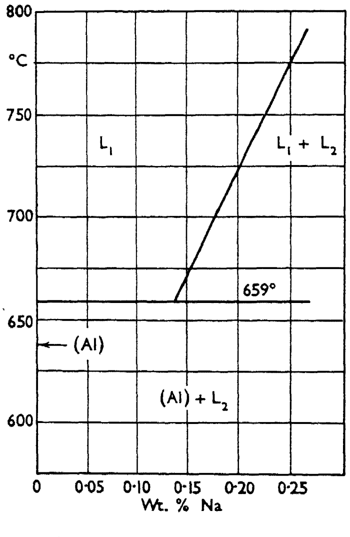

FIG. 17. EQUILIBRIUM DIAGRAM Na–Al

The presence of sodium up to 0·04% does not affect the physical and mechanical properties of aluminium to any significant extent. Above this limit the hardness and electrical conductivity are decreased and intercrystallization corrosion occurs.[283]

The solubility of sodium in aluminium–copper alloys containing 8% copper is 0·15% at 700°C., 0·18% at 800°C.[280]

The effect of sodium on the tensile properties of aluminium–copper alloys has been studied by Claws and Goederitz and is found to be in general detrimental.[284]

Lugaskov[139] also discusses the influence of sodium on the properties of aluminium alloys.

An aluminium–germanium alloy prepared from 99·96% aluminium and containing 65 wt.-% of germanium has been treated with 1 wt.-% of sodium at 700°C. In addition to the usual modification effect a new phase is found in the cooled alloy; it is light-grey, somewhat darker than germanium, has a fibrous structure, resists attack by the usual acids and is similar to the corresponding phase in aluminium–silicon–sodium alloys.[285]

The solubility of sodium in aluminium–magnesium alloys containing 5% of magnesium is about 0·17% at 700°C. and 0·21% at 800°C. A dark grey to black sodium-rich microconstituent is found in these alloys.[280]

The sodium–aluminium–silicon system has been investigated by Nowotny and Scheil.[286] Sodium is fused with an aluminium–silicon alloy in a clay crucible and sodium aluminium silicide obtained. It is greyish-blue in appearance with a metallic lustre and its composition is 15·3 Na, 18·0 Al, 66·7 Si expressed as at.-%; this composition corresponds to the formula $NaAlSi_4$ or $(NaAl)Si_2$, a disilicide. It crystallizes in a tetragonal cell with $a = 4{\cdot}13$A. and $c = 7{\cdot}40$A. with six atoms per unit cell.

The solubility of sodium in aluminium–silicon alloy containing 13% Si, 0·4% Fe and 0·1% Ti is 0·08% at 600°C., 0·12% at 700°C., 0·125% at 750°C. and 0·11% of sodium at 800°C.[280]

When aluminium containing silicon in solid solution is heated in liquid sodium a ternary compound is formed as a surface layer or sub-scale. The equilibrium silicon contents at 600°, 550°, 500° are 0·15%, 0·04% and 0·01% respectively while the corresponding sodium contents are in the range 0·0016–0·0005%. The compound is stable to high temperature, *i.e.* above 800°C. Only one compound has been observed and its composition appears to be $(NaAlSi_{1\cdot25})$ or $(NaAlSi_{1\cdot33})$. A tentative diagram for the aluminium–silicon–sodium system has been prepared indicating a ternary eutectic at about 0·017% of sodium.[282]

Otani states that thermal analysis shows that sodium prevents undercooling of the aluminium–silicon eutectic (12·2% Si at 578°) and gives a third heat evolution during cooling. The ternary equilibrium diagram is discussed and photomicrographs are given. It is assumed that sodium forms an immiscible liquid with silicon as well as aluminium and that a sodium-rich liquid isolates the growing crystals from the mother liquor and prevents their becoming coarse as in a pure aluminium–silicon alloy.

Much work has been done on the effect of the addition of sodium on the physical and casting properties of aluminium–silicon alloys.

Alloys containing 8–14% of silicon and modified by the addition of sodium are apt to be unsound but sodium chloride or fluoride gives better and more uniform improvements in mechanical properties.[288]

The action of sodium or alkali metal compounds as modifying agents is considered by Gwyer and Phillips to be due to their function as colloid protectors, so that aggregation of silicon and aluminium particles is retarded. Thermal arrests are lower and more gradual in the modified alloys and this is considered to be due to a reduction in the speed of crystallization by the presence of the modifiers.[289]

The refinement of aluminium–silicon alloys by the addition of sodium is also discussed by Archer and Kempf.[290] Metallic sodium is considered to give as good and as uniform a modification as a salt flux, but it is important that the molten alloy should contain a definite amount of sodium at the moment of casting, the amount varying with the silicon content. For all compositions described both strength and elongation are improved by modification.[291]

The absolute viscosities, η, of aluminium–silicon alloys containing up to 19% of silicon have been determined by photographically recorded logarithmic decrements of torsional oscillations of a steel sphere suspended on a steel wire. Modification of Silumin by addition of 0·1% sodium raises η to such an extent that oscillation is at first suppressed altogether; after 5-7min. η is still 15 times higher than for pure Silumin and continues to decrease over 40 min. Addition of sodium to aluminium has a similar effect. The action of sodium is explained as adsorption at the interface of crystallization germ and melt which results in inhibition of crystal growth and production of finer grain size.[292]

According to Boom[293] silicon crystals grow from an aluminium–silicon 12–13% eutectic in the form of thick lamellae radiating from the centre of a spherulite. In the presence of sodium this growth is perturbed by growing aluminium dendrites, and silicon forms scattered fine crystals. Zednik[294] states that the addition of an excess of sodium to aluminium–silicon alloys can be as detrimental to the casting as a deficiency. Schultz has established that 0·0066–0·0088% of sodium is an optimum amount to add for improvement in soundness, structure and mechanical properties in chill and sand castings. Small losses of sodium occur between addition to the molten metal and casting.[295] Small additions of sodium result in a decrease of the temperature of the aluminium–silicon eutectic, a phenomenon of undercooling.[296,297] The sodium content adequate with chilled castings is lower than with sand castings and the molten alloy should be poured quickly after the addition of sodium which may be lost in a few minutes. The effect of the addition is to decrease the grain size of the eutectic.[297] In the preparation of eutectic aluminium–silicon alloys through thermal reduction with carbon, 2–10% of sodium is added to the molten alloy by pressure-injection just above the eutectic temperature under an inert atmosphere, whereby excess silicon is eliminated in the form of large crystalline plates.[298] Many other references have been made to the improvement of aluminium–silicon alloys by the addition of sodium.[299-303]

To avoid explosions when introducing sodium to the above alloys it is recommended that it should be wiped free from the petroleum in which it has been stored and covered with aluminium foil, which is then hammered to expel air, before plunging the wrapped sodium into the molten alloy.[304]

Sodium retards the sintering of alumina.[305]

The system lanthanum–sodium has been examined by Mässenhausen;[306] the components show but little mutual affinity and a gap in mutual solubility is found.

Gallium is only slightly miscible with sodium.[107] Gilfillan[307] gives a value of 0·001% by weight for the solubility of sodium in gallium at 30°C.

Indium is slightly miscible with liquid sodium, forming a eutectic which melts at about 96·1°C. and contains 1·2–2·0% of indium. There is some evidence of the formation of the compound NaIn.[1]

Zintl and Neumayr[308] have prepared the compound NaIn and examined its crystal structure. It is grey in colour, m.p. about 500°C., sensitive to air and has *d* 4·70. An *X*-ray powder diagram shows that the compound has the same structure as NaTl, *i.e.* the co-ordinates of the atoms are those of a body-centred cubic lattice; the arrangement of the two kinds of atoms, sodium and indium, being such that the four nearest neighbours of each atom are of the other kind. Owing to the very low co-ordination number, the interatomic distances in alloys with this structure are very much shorter than the sums of the radii derived from the structures of the pure metals. The lattice constant is 7·297A. ± 0·005; the radius of sodium in the compound is 15% smaller than in the free metal:-

$$r^{[8]}_{Na} = r^{[8]}_{In} = 1{\cdot}58\text{A. whereas } r^{[8]}_{Na} \text{ in the free metal} = 1{\cdot}86\text{A.}$$

The number of atoms per unit cell is 16·01.

In the recovery of indium from indium oxide, In_2O_3, by electrolysis of the oxide in fused sodium hydroxide, a fused alloy of sodium-indium is first formed, m.p. 725–50°F.[309]

An extensive literature survey of the binary alloys of indium with many metals including sodium has been prepared by Valentiner.[310]

A sodium-indium alloy containing 0·1 mole fraction of sodium injected into dry air at 700°C. and 1 atm. is quite reactive.[132]

Reactions of thallium salts with sodium in liquid ammonia, already described (see page 514) give evidence for the existence of the compounds NaTl, $NaTl_2$ and Na_3Tl_2. Kremann and Reiningshaus[152] using cells of the type Tl | $1N.Na_2SO_4$ | $Tl_{1x}Na_x$ in water, find that for concentrations of 0–50% of thallium in sodium the e.m.f. is practically the same as that for pure sodium but that above 50% of thallium a sudden drop in potential of over 480mV. occurs. It is assumed that this is due to the formation of the compound NaTl, but no evidence is obtained for the existence of the compounds Na_2Tl and Na_5Tl.

Grube and Schmidt[311] have investigated the sodium-thallium system by thermal analysis and temperature-resistance measurements. The complete phase diagram shows the compounds $NaTl_2$, NaTl, Na_2Tl and Na_6Tl. The compound NaTl melts at 305°C. without decomposition; $NaTl_2$ is formed from alpha- and gamma- mixed crystals in the solid state at 154°C. Na_2Tl and Na_6Tl are formed by peritectic reaction from gamma- mixed crystals and Na_2Tl crystals respectively and melt at 154° and 77·4°C. respectively. Alloys containing 17–24 at.-% of sodium can be tempered; by heating at 200°C. and quenching the hardness is increased by 50–60%. Clearly marked eutectic points on the freezing point curve are shown at 238° (37·3 at.-% Na) and 63·9° (92·9 at.-% Na).

The solubility of thallium in sodium down to 64°C. is given by the expression:-

$$\log(1 - W/100) + 2{\cdot}2917 - 849{\cdot}5/T$$

where W = wt.-% of thallium and T = °K.[1]

A phase diagram[125] is shown in Fig. 18.

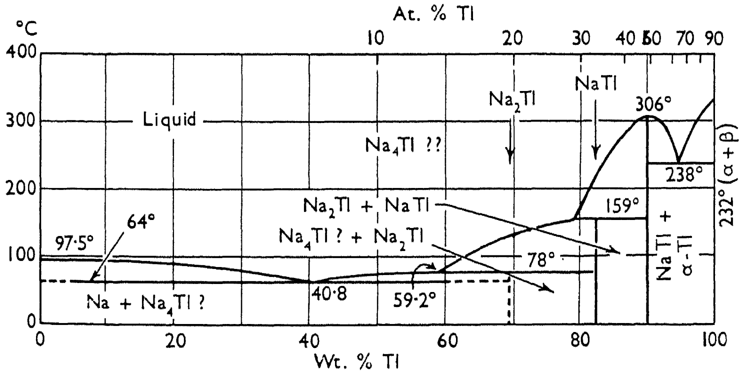

FIG. 18. EQUILIBRIUM DIAGRAM Na-Tl

Heymann and Weber[312] have shown that compounds of sodium with thallium are stable up to about 200° above their m.p. but decompose at higher temperatures.

Activities and activity coefficients of sodium in thallium have been calculated[313] from e.m.f. measurements using a cell containing sodium and sodium–thallium alloys separated by a glass partition. The difference between the real and ideal chemical potential, *i.e,* RTlnfNa, where fNa is the activity coefficient of sodium in thallium, shows considerable departure from Raoult's law.

The crystal structure of the compound NaTl is a special case of the cubic space centred beta brass structure, each atom having four nearest neighbours of the other kind. The side of the lattice, $a = 7{\cdot}473$A. and there are 16 atoms per unit cell. The interatomic distances are 13% shorter than the sums of the radii derived from the structures of the pure metals:-

$$r_{Na}^{[8]} \text{ in the free metal} = 1{\cdot}86\text{A. whereas } r_{Na}^{[8]} \text{ in NaTl} = 1{\cdot}62\text{A.}$$

The compounds LiZn, LiCd, LiGa, LiIn and NaIn all have the same structure.[314]

The following thermochemical data have been given by Kubaschewski and Catterall:-[38] ½NaTl:ΔH_{298} = -4500 ± 300g.-cal.; $\Delta V_{298} = -0{\cdot}23$; *Lf* (latent heat of fusion) = 2000 ± 50g.-cal. (250–305°). There appears to be a rapid increase of $\overline{C_p}$ from 250°C. upwards, possibly due to the loosening of the covalent bonds, and if this is taken into account, *Lf* is reduced to 1270g.-cal. /g.-atom. The partial heats of solution ΔH_{Na} and partial free energies ΔG_{Na}, *i.e.* change in heat content and change in free energy when 1g.-atom of sodium is assimilated by a (theoretically) infinite amount of an alloy of constant composition N_{Na}, are given in Table XLIV expressed as calories.

TABLE XLIV. THERMOCHEMICAL DATA FOR THE SODIUM–THALLIUM SYSTEM

N_{Na}	ΔG_{Na} (648°K.)	ΔH_{Na}
0·2	-9500	-
0·3	-5810	-6300
0·4	-4000	-4270
0·5	-2500	-2800
0·6	-1400	-1600
0·7	-710	-810
0·8	-320	-410
0·90	-120	-140

The atomic volume of liquid NaTl is 18·23 at the m.p. corresponding to a volume change on formation ΔV_{578° of $-0{\cdot}175$ where:-

$$\Delta V_{578^\circ} = [V(\text{alloy}) - \Sigma V(\text{metals})]/\Sigma V \text{ metals at } 578^\circ\text{K.}$$

Nuclear magnetic resonance experiments carried out with a sodium–thallium alloy, NaTl, shows a negative shift of -1%.[315]

Wagner has calculated the change in the activity coefficient of sodium with concentration of thallium in the sodium–thallium–mercury system by means of the expression $d\ln\gamma_{Na}/dx_{Tl} = d\ln\gamma_{Tl}/dx_{Na}$ where γ is the activity coefficient and x the molar fraction. For the binary system Hg–Tl, $d\ln\gamma_{Tl}/dx_{Tl} = 13{\cdot}1$ and for the system Hg–Na, $d\ln\gamma_{Na}/dx_{Na} = 36{\cdot}0$. From these values:-

$$d\ln\gamma_{Na}/dx_{Tl} = \left[\frac{d\ln\gamma_{Na}}{dx_{Na}}\cdot\frac{d\ln\gamma_{Tl}}{dx_{Tl}}\right]^{1/2} = 21{\cdot}8.$$

An experimental value has been obtained by determining the e.m.f. of galvanic cells of the type: (Hg, alkali metal) | alkali hydroxide (aq.) | (Hg, alkali metal, Tl) and measuring the slope of the lines in the plot, e.m.f. (corrected)/mol. fraction of thallium. The value of $d\ln\gamma_{Na}/dx_{Tl} = 22{\cdot}1$ which is in good agreement with Wagner's calculated result.[120]

Titanium, zirconium, uranium and boron alloys with aluminium or other base alloys may be obtained by reducing the metal halides with sodium in the presence of the alloying metal. For high melting compounds such as iron-titanium and iron-zirconium the halides may be first reduced with sodium and the base metal added to the fused mixture.[137]

Kremann and Gmachl-Pammer[316] by e.m.f. measurements for cells of the type Sn/0·1N. NaI solution in pyridine/Sn_xNa_{1-x} and Sn/N. Na_2SO_4, aq./Sn_xNa_{1-x}, the latter for alloys containing <67 at.-% of sodium, have obtained evidence for the existence of the following compounds: Na_4Sn, Na_2Sn, NaSn and $NaSn_2$ but not for Na_4Sn_3.

Hume-Rothery[317] has prepared an equilibrium diagram on which the following compounds appear: Na_4Sn m.p. 408°C.; Na_3Sn; Na_2Sn m.p. 487°C.; Na_4Sn_3 m.p. 479°C.; NaSn m.p. 578°C.; $NaSn_2$; $NaSn_3$; $NaSn_4$ and $NaSn_6$. All are metallic but decompose on melting, except where the m.p. is given. Na_4Sn_3 is stable above 357°C.; below this temperature it decomposes into Na_2Sn and NaSn, the reverse process taking place above 357°C. Na_3Sn decomposes into Na_4Sn and Na_2Sn above 377°C. $NaSn_2$ is formed from a reaction between NaSn and liquid tin at 307°C.; $NaSn_3$ from $NaSn_2$ and liquid at 289°; $NaSn_4$ from $NaSn_3$ and liquid at 229°C., and $NaSn_6$ from $NaSn_4$ and liquid at 226°C. No evidence is obtained for the formation of solid solutions.

The compound Na_2Sn is a blue-black crystalline solid which dissolves in water leaving a tin skeleton.[318]

Zintl and Harder, by melting tin and sodium together and extracting excess sodium with liquid ammonia, have obtained crystals of the compound $Na_{15}Sn_4$, rhombic in structure with $a_1 = 9{\cdot}79$, $a_2 = 22{\cdot}78$, $a_3 = 5{\cdot}56$A. and with 38 atoms per unit cell. This compound has been previously described as Na_4Sn.[319]

The phase diagram[125] is shown in Fig. 19.

Reactions of tin, tin salts, and sodium-tin alloys in a liquid ammonia solution of sodium have already been described (see page 516). The compound Na_4Sn_9 forms a deep-red solution.

The solubility of tin in sodium is given by the expression $W = 7{\cdot}9 - 0{\cdot}141t + 6{\cdot}16 \times 10^{-4}t^2$ where W = wt.-% and t is °C.[1]

A high-temperature calorimeter has been used for the determination of heats of formation of sodium-tin alloys at 880°K. by McKisson and Bromley.[320] The authors, comparing their results with those of other workers as shown in Table XLV, find that these tend to support those of Kubaschewski and Seith.[165]

TABLE XLV. HEATS OF FORMATION OF SODIUM-TIN ALLOYS

Composition	ΔHf kg.-cal. per g.-atom	Temp. °K.	References
$NaSn_2$	−5	298	321
	−6·7	298	164, 322, 323
	−3·65 ± 0·25	880	320
NaSn	−5·5	298	321
	−8	298	164, 322, 323
	−6	Room	165, 324, 325
	−4·9 ± 0·2	873	326
	−4·8 ± 0·14	882	320

continued on following page

TABLE XXLV. (continued)

Composition	ΔHf kg.-cal. per g.-atom	Temp. °K.	References
Na$_{1\cdot105}$Sn	−4·86 ± 0·04	881	320
Na$_4$Sn$_3$	−5·1 −8 −4·65 ± 0·3	298 298 880	321 164, 322, 323 320
Na$_2$Sn	−4 −7 −4·8 −4·03 ± 0·08	298 298 Room 885	321 164, 322, 323 165, 324, 325 320
Na$_4$Sn	−4·2 −6·8 −2·9 −2·5 ± 0·5	298 298 298 880	321 164, 322, 323 165, 324, 325 320

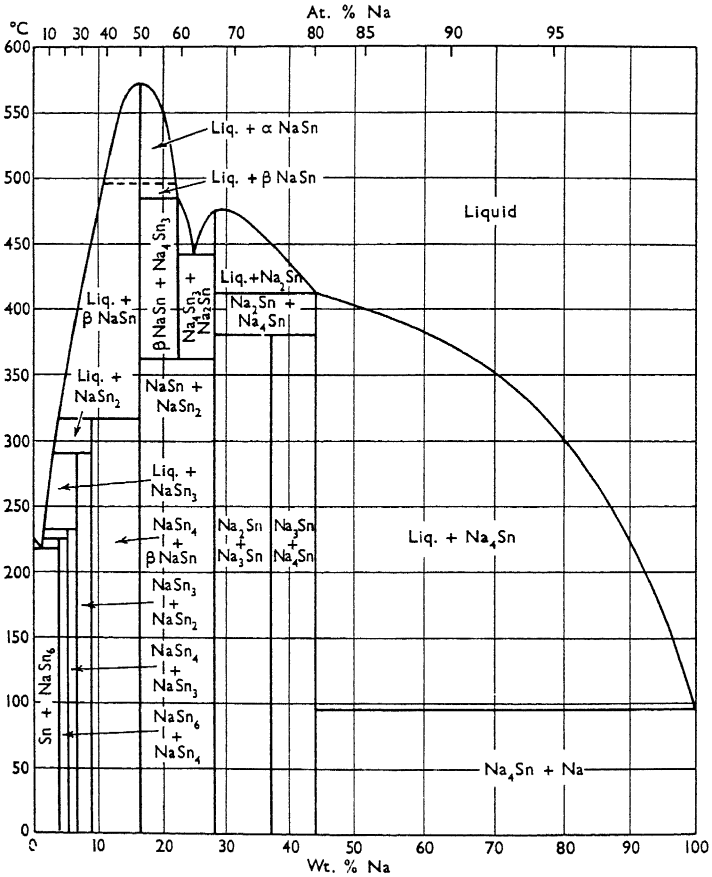

FIG. 19. EQUILIBRIUM DIAGRAM Na-Sn

Hauffe and Vierk[313] with a cell containing a glass partition between sodium and sodium-tin alloys have measured the e.m.f. values at 480°C. for alloy compositions of 26·7–85·1 at.-% of sodium. Sodium activity coefficients, f_{Na}, and the values of $RT \ln f_{Na}$ calculated from their results indicate that there is considerable departure from ideal behaviour.

Kubaschewski and Catterall,[38] having critically reviewed the recorded thermochemical data, give values for the heats of formation of the solid compounds, ΔH sol. g.-cal./g.-atom, heats of formation in the liquid state ΔH liq., the partial free energy $\bar{G}$Me and the entropies of mixing ΔS liq. as shown in Table XLVI. The integral values apply to the formation of 1g.-atom, of alloy from the atomic fractions of tin and sodium. The data shown in column 5 indicate the formation of a new, presumably polar, bond between mixtures of sodium and tin which would account for the relatively high negative heats of formation and mixing.

TABLE XLVI. THERMOCHEMICAL DATA FOR SODIUM-TIN ALLOYS

N_{Sn}	ΔH sol.	ΔH liq.	$\Delta\bar{G}$(Na) liq.	ΔS liq.
0·20	−2700	−2500	−600	+0·40
0·333	−4800	−4030	−1820	−0·17
0·428	−5400	−4650	−2820	−0·34
0·50	−6000	−4800	−3800	−0·32
0·667	−400	−3650	−7300	+0·82

An early reference to the type of apparatus suitable for the preparation of alloys of sodium with tin or lead is given by Kraus and Callis.[327]

Sodium-tin alloys containing 0·1 mol. fraction of sodium when heated and injected into dry air at 700° C. and 1atm. react vigorously.[132]

Sodium-tin alloys can be substituted for either tin or sodium in reversible glass-tin-sodium reference electrodes in fused salts to give smaller voltages.[328] Delimarskii and Kollotti[329] have measured the e.m.f. of cells of the type Na/glass/Na_xSn_{1-x},aq. and give values for alloys containing 6·2–60 wt.-% Na at temperatures of 450°–600°C. Below 40% of sodium the temperature coefficient of the e.m.f. is negative. The data, given in Table XLVII, are considered to be useful for reference electrodes at high temperatures.

TABLE XLVII. ELECTROMOTIVE FORCE OF SODIUM IN SODIUM-TIN ALLOYS

Wt.-% Na	Temp. °C.	E.M.F., V.
6·2	450	0·3858
	500	0·3822
	510	0·3814
7·75	500	0·3630
	600	0·3560
17·88	590	0·2113
	650	0·2058
24·38	460	0·1072
	500	0·1068
	510	0·1067
30·67	500	0·0669
	560	0·0058
39·72	500	0·0430
	620	0·0360
44·72	490	0·0247
	500	0·0249
	540	0·0253
50·93	450	0·0140
	500	0·0155

continued on following page.

TABLE XLVII (continued)

Wt.-% Na	Temp. °C.	E.M.F., V.
	520	0·0160
58·50	460	0·0080
	500	0·0090
	530	0·0096
60·00	450	0·0065
	500	0·0083
	530	0·0087

A method for the production of sodium from soda-ash by reaction with coke involves the removal of sodium vapour from carbon monoxide by solution in molten tin, the sodium-tin alloy being then distilled to recover sodium.[331]

Measurements[152] of the e.m.f. of cells of the type Pb/0·1N. NaI/Pb_xNa_{1-x} in pyridine and water and Pb/N. Na_2SO_4/Pb_xNa_{1-x} in water, the latter for alloys containing 70–100% of lead, show that from 0–20% of lead the potential is practically the same as that for pure sodium. The compounds NaPb and Na_2Pb_5 are clearly distinguished by their potentials, which are 650 and 1500 mV. "nobler" than sodium, but there is no definite evidence of the existence of the compounds Na_4Pb and Na_2Pb described by earlier workers. A corrected f.p. diagram[332] shows that the pure compound separating from alloys of compositions 58·8–76·6 at.-% of sodium is Na_5Pb_2, and that this forms solid solutions with both NaPb and Na_4Pb. On cooling, alloys containing 58·8–71·4 at.-% Na rearrange at 182°C. when Na_5Pb_2 disappears and Na_2Pb is formed.

According to Goebel[333] the limit of the solid solution is 0·80% of sodium; Na_2Pb is formed at 4% Na and 320°C.; NaPb at 9·8% Na and 365°C. There is a eutectic at 6·2% Na and 310°C. The specific gravity of cast alloys containing 0–1·6% Na is slightly higher than that of slowly cooled alloys; generally slow cooling increases hardness by 10–30%. Hardness curves show a sharp rise to a maximum at 2% Na, a slow fall to a minimum at 4% (Na_2Pb_5), a second maximum at 6·2% and minimum hardness at 9·8%. The hardness of a 0·55% sodium alloy is increased 10–15% on quenching at 100–310° and standing 24 hr. Corrosion of these alloys increases with sodium content and only those containing less than 0·78% Na are considered to be commercially important.

The saturation limit of alpha-lead sodium crystals is stated by Czochralski[334] to be higher than 0·8% of sodium as found by Goebel[333] since microphotographs show completely homogenized solid solutions containing 1·28–1·59% Na. According to Kurnakov and Pogodin[335] the limit of the solubility of sodium in lead reaches 1·9% at the eutectic temperature and is only 0·4% at 20°C. Klaiber[336] gives higher values, 18 at.-% Na at the eutectic temperature, 3·5 at.-% at 20°C.; other values given are 13·3 at.-% at 290°C., 5 at.-% Na at 20°[337] and 1·37 wt.-% at 290° and 0·45% at room temperature.[338]

Reactions of lead salts in liquid ammonia, affording indications of the existence of the compounds Na_4Pb_7 and Na_4Pb_9, have already been described (see page 516).

Extraction of suitable sodium-lead alloys with liquid ammonia gives solutions of salt-like ammines, Na_4Pb_9,xNH_3 where $x = 9$, 8, 6 and 5. By removal of ammonia alloy phases are obtained identical with those formed from molten alloys. The alpha phase has a lattice constant, a = 4·932A. whereas that of pure lead is 4·943A., although the sodium atom is larger than the lead atom. Beta phase alloys with 28–32 at.-% of sodium have a lattice side of a = 4·873A., with 4 atoms per unit cell.[339]

The structure of the compound already referred to as Na_4Pb has been investigated by Stillwell and Robinson[340] whose diffraction data indicate the formula Na$_{31}$Pb$_8$, but Zintl and Harder have shown that it is in fact Na$_{15}$Pb$_4$.[319]

Kurnakov and Pogodin[335] have found that at compositions 3·5–5·5% Na the beta-phase is of variable composition and is not the compound Na$_2$Pb$_5$ as previously reported. The complete phase diagram given by Klaiber[336] shows the compounds NaPb, Na$_2$Pb, Na$_5$Pb$_2$ and Na$_4$Pb (see above, Na$_{15}$Pb$_4$). The homogeneous region of the beta-phase (not, as earlier reported, the compound Na$_2$Pb$_5$) is found to be at 20°C. between 27·7 and 32·5 at.-% Na and at 298°C. between 27 and 32·5 at.-% Na. Makarov and Popova[341] find that the beta-phase exists between 26·5–35·1 at.-% Na at room temperature. The lattice constant decreases from 4·870 to 4·861A. with increasing sodium content and the density from 8·79 to 7·49 with an especially rapid fall at 35 at.-% Na. Up to about 33 at.-% Na the number of atoms per unit cell is calculated as 3·95 but at 35 at.-% is only 3·65.

The region of the phase diagram in the vicinity of the composition Na$_9$Pb$_4$ has been reinvestigated by Krohn *et al.*[342] by thermal and microscopic analysis, and the compound Na$_9$Pb$_4$, unrecognized by earlier thermal analysis, found to be present. The phase Na$_5$Pb$_2$ has been shown to be a peritectic compound. The 190° isothermal curve represents an order-disorder change involving Na$_9$Pb$_4$.

The wt.-% of lead in sodium up to 40% lead (250°C.) is given by the expression: $W = -25{\cdot}6 + 0{\cdot}262t$ where W = wt.-% and t = °C.[1]

The phase diagram[125] is shown in Fig. 20.

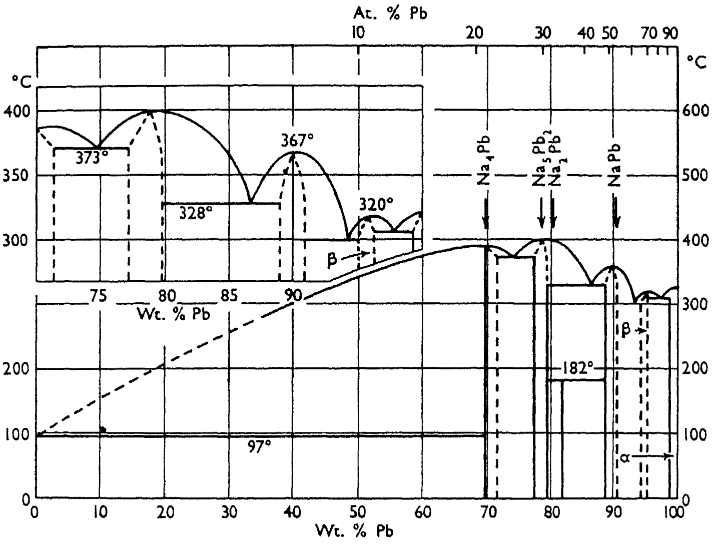

FIG. 20. EQUILIBRIUM DIAGRAM Na–Pb

Kubaschewski and Catterall[38] in their collection of thermochemical data list the compounds of sodium–lead as: Na$_{31}$Pb$_8$, Na$_5$Pb$_2$, Na$_2$Pb, NaPb and NaPb$_3$. In the liquid state sodium and lead are described as completely miscible.

Measurements of e.m.f. for cells such as Na/glass/Na$_x$Pb$_{1-x}$ at 425° and 475°C. have been made by Hauffe and Vierk[313] and from the results activities and activity coefficients of sodium and $RT\ln f$Na values, where fNa is the activity coefficient, calculated. As for sodium–thallium and sodium–tin alloys, wide departure from ideal behaviour is apparent. The results for two of the alloys, the richest and poorest in sodium, are given in Table XLVIII to show the order of values obtained: αNa = activity of Na; fNa = activity coefficient; xNa = atom fraction of Na where $(1 - x)$ = atom fraction of lead.

TABLE XLVIII. ELECTROMOTIVE FORCE AND ACTIVITIES OF SODIUM IN SODIUM-LEAD ALLOYS

Cell	xNa	E.M.F. (mV.)	αNa	fNa	$RT \ln f$Na (cal.)
xNa/Glass/Na at 425°	0·935	5·0	0·920	0·983	−25·4
	0·392	288·5	0·008	0·021	−5316·0
xNa/Glass/Na at 475°	0·935	5·0	0·925	0·989	−17·0
	0·392	287	0·011	0·029	−5240·0

Porter and Feinleib[343] have measured the activities and activity coefficients of sodium in lead by e.m.f. measurements of cells of the type Na(pure)/Na^+/Na in Pb at temperatures up to 820°C. Extrapolation to 1010°C. gives values shown to be of the right order by a few "check" experiments.

Results are given in Table XLIX for an alloy containing 2·90 wt.-% Na *i.e.* N_{Na} = 0·212 as typical of the whole series ranging for N_{Na} from 0·151 to 0·401.

TABLE XLIX. ELECTROMOTIVE FORCE AND ACTIVITIES OF SODIUM IN SODIUM-LEAD ALLOYS

Temp.		E.M.F.	Activity (Na)	Activity Coefficient (Na)
°C.	°K.	(mV.)	$\times 10^{-3}$	$\times 10^{-2}$
827	1100	389	16·5	7·78
798	1071	393	14·2	6·70
763	1036	398	11·6	5·47
730	1003	400	9·77	4·61
695	968	405	7·78	3·67
664	937	408	6·38	3·01
622	895	409	4·98	2·35
552	825	409	3·17	1·50
502	775	404	2·36	1·11

The data, based partly on a critical survey of earlier work, given by Kubaschewski and Catterall[38] are recorded in Table L where N_{Pb} = atom fraction of lead; ΔH refers to heat of formation in g.-cal./g.-atom (*i.e.* N_{Pb} g.-atom of lead + 1 − N_{Pb}g.-atom of sodium) ΔV_{298} = volume change on formation; Lf = latent heat of fusion in g.-cal./g.-atom; $\Delta\overline{G}_{Na(liq.)}$ = partial free energy g.-cal.

TABLE L. THERMODYNAMIC DATA FOR SODIUM-LEAD ALLOYS

N_{Pb}	ΔH_{293} solid	ΔV_{298} solid	Lf	$\Delta G_{Na(liq.)}$748°K.
0·20	−4000	−0·197		−950
0·286	−5000	–		−1940
0·333	−5200	−0·169	(−1700)	−2480
0·50	−5800	−0·143	(−1950)	−4650
0·714	−3300	−0·105	(−1700)	(−8900)

Sodium-lead alloys show age-hardening effects;[335] the Brinell hardness increases with the percentage of sodium and can attain 190% of the original value by tempering.[336] The influence of high cooling rates on the solidification and structure of binary alloys has been studied: with sodium-lead alloys segregation occurs within several days at room temperature.[344] The increase in hardness of sodium-lead alloys during 50 days ageing at 20°C. is due to the fine state in which the other crystal types separate from the supersaturated mixed crystals.[345] Thieme[346] gives microphotographs showing the hardening effects of various elements, including sodium, on lead.

When sodium-lead alloys contained in narrow-bore tubes are electrolyzed and the tubes are subsequently broken up, and the contents analyzed, it is found that the alloy around the cathode is enriched with sodium and that around the anode with lead.[347]

When molten sodium-lead alloy is injected into air at 700°C. and 1atm. pressure it reacts producing flame and dense smoke, although the time of flight is too small for complete reaction to occur.[132]

Sodium-lead alloys containing more than 2% Na react with the water of the air.[348]

The oxidation and hydration of a hot sodium-lead alloy is prevented by the presence of an atmosphere of vapours from a hydrocarbon oil, flash point above 300°C.[349]

Various procedures have been described for the production of sodium-lead alloys. An amalgam is prepared by electrolysis of an alkali metal salt with a mercury cathode, lead is then added to the amalgam and the mercury is distilled off.[350,351] The electrolysis of fused alkali metal chloride may be used to manufacture sodium-lead alloys.[352] A molten lead cathode and graphite anode used to electrolyze a mixture of sodium chloride and potassium fluoride at 600°C. yield a sodium-lead alloy containing 0·8% of sodium. In such reactions glass vessels are attacked by the melt but sintered alumina is satisfactory.[354] Electrolysis of fused sodium salts with a lead cathode gives sodium-lead alloys which may be distilled or electrolyzed to produce sodium.[355] Homogeneous alloys of sodium and lead are obtained by using an extrusion press at a temperature of 260–330°C. and a pressure of 800–3000kg. per sq. cm.[356,357]

There are numerous references in the literature to the preparation of sodium-lead alloys for the production of alkylated lead compounds.[359,360-369] Uniform small granules, practically free from dust, are obtained by constantly agitating a fused sodium-lead alloy while cooling, in the absence of moisture and oxygen, to a temperature below that at which the particles tend to adhere.[359] Alloys suitable for the preparation of lead alkyls contain sodium 10, lead 89·95–89·0 and magnesium 0·5–1·0%.[360] The addition of magnesium to sodium-lead alloys results in high yields of tetraethyl lead, tetramethyl lead, dimethyldiethyl lead and triethylphenyl lead on treatment with alkylating reagents in the presence of a catalyst.[361] Ternary alloys of sodium-lead-magnesium containing up to 22·5% sodium and 2·5–25% of magnesium may be used as the source of lead in the reaction[370] or ternary alloys containing sodium 0·5–15% and magnesium 3–19·5%, the rest lead.[363,371]

The maximum reactivity of a sodium-lead alloy is attained when the solidification time does not exceed 30 sec.[364] An exceptionally active alloy is prepared by depositing a thin layer of molten mono-sodium-lead alloy on a metal surface, preferably one containing an appreciable amount of copper, such as bronze.[372] The highest yields of tetraethyl lead are obtained when the atomic ratio of alkali metal to lead is nearly 1:1,[365] and the relation between the yield and the proportion of lead in the alloy shows a sharp maximum at 79–80% of lead.[366] Various methods and devices, including the use of catalysts, have been described for the production of lead alkyls, especially tetraethyl lead.[365,366,368,373,374,377]

Steel wire or strip may be coated with sodium-lead alloy containing 3–7% sodium by applying the molten alloy at a temperature of 340–380°.[378]

A sodium-lead alloy (5% Na) is suggested for the recovery of gold from cyanide solutions, the lead-gold alloy obtained being dried and cupelled directly. The sodium-lead alloy produced by electrolyzing fused sodium chloride over a molten lead cathode is brittle, easily powdered and reacts slowly with water without explosion.[379]

Sodium-lead alloys are used to reduce organic compounds giving results similar to those of electrolytic reduction with lead electrodes.[380-384]

Arsenic is miscible with sodium in all proportions.[1] The compounds formed by sodium with arsenic have already been described (see page 511).

Sodium removes arsenic from alloys, acting as a cleanser, but the formation of sodium arsenide may be hazardous owing to the production of arsine on exposure to moist air. Kroll[137] refers to procedures whereby this danger may be reduced; e.g. the addition of sodium hydroxide after the addition of sodium to impure lead causes oxidation of arsenide and antimonide *in situ*. Alternatively the dross containing arsenide or antimonide may be treated with superheated steam and the arsine cracked to metal and hydrogen above 500°C. or burned with excess air to arsenic oxide.

The reactions of sodium with antimony or its salts in liquid ammonia have already been described (see pages 512).

Antimony and sodium are miscible in all proportions.[1] Kubaschewski and Catterall give the data reported in Table LI for the two compounds, Na_3Sb and NaSb,[38] where ΔH_{298} is expressed as g.-cal. per g.-atom.

TABLE LI. PROPERTIES OF THE SODIUM ANTIMONIDES

Compound	m.p.	ΔH_{298}	ΔV_{298}
$\frac{1}{4}Na_3Sb$	856	-11,800 ± 800	-0·18
$\frac{1}{2}NaSb$	465	-7,900 ± 500	-0·157

The phase diagram[125] is shown in Fig. 21.

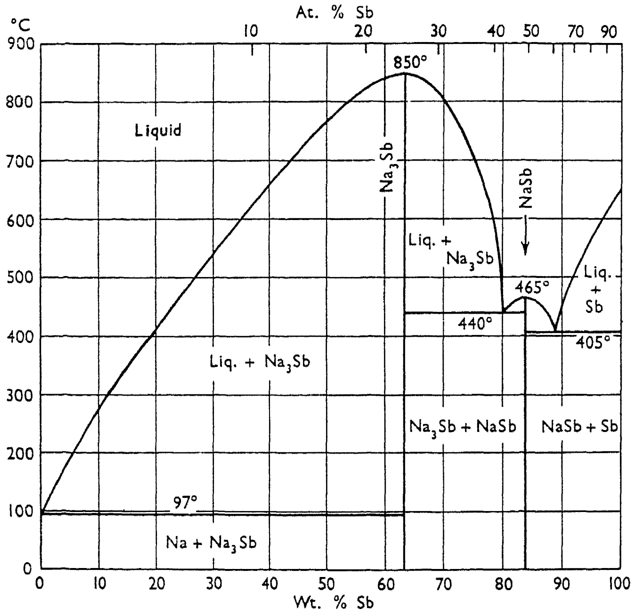

FIG. 21. EQUILIBRIUM DIAGRAM Na-Sb

Compounds of sodium and bismuth formed in liquid ammonia have already been described (see pages 513). Kremann and Pressfreund have measured the e.m.f. of sodium-bismuth alloys.[385]

Bismuth and sodium are miscible in all proportions and the solubility of bismuth up to 600°C. *i.e.* 40% Bi in sodium is given by the expression: W =

$-0{\cdot}0129t + 1{\cdot}33 \times 10^{-4}t^2$, where W = wt.-% and t = °C.[1] Kubaschewski and Catterall give the data recorded in Table LII for the two compounds of bismuth Na_3Bi and NaBi.[38]

TABLE LII. PROPERTIES OF SODIUM BISMUTHIDES

Compound	m.p. °C.	ΔH_{298} g.-cal./g.-atom	ΔV_{298}
$\frac{1}{4}Na_3Bi$	775	$-11{,}400 \pm 700$	$-0{\cdot}135$
$\frac{1}{2}NaBi$		$-7{,}600 \pm 500$	$-0{\cdot}18$

Measurements of the surface tension of bismuth and its alloys with sodium containing 0·027–0·664 at.-% of sodium between 260° and 500°C. show that sodium lowers the surface tension of bismuth. The maximum adsorption calculated by Gibbs equation is much smaller for sodium than for potassium and decreases with rising temperature.[386] The microhardness of the alloys increases as the surface tension is lowered by the addition of alkali metal.[387] The compound BiNa has been found by Alekseevskii[388] to exhibit superconductivity at 2·25°K. but the compound $BiNa_3$ is not superconducting down to 1·4°K.[389]

The phase diagram[125] is shown in Fig. 22.

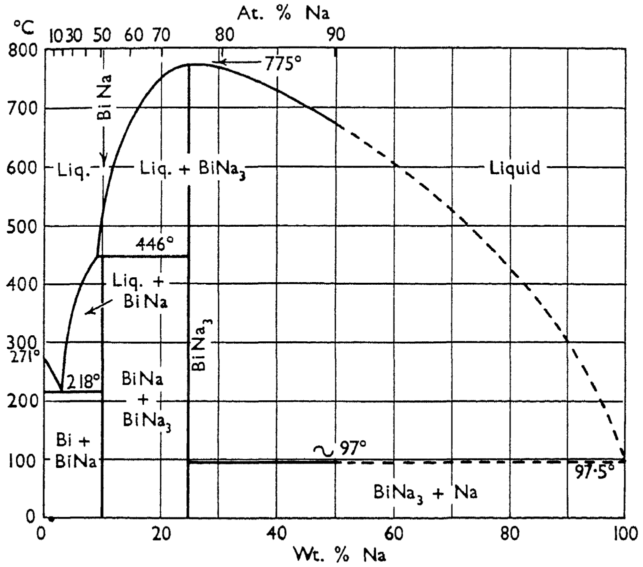

FIG. 22. EQUILIBRIUM DIAGRAM Na–Bi

Sodium–thorium alloys have been prepared by melting the metals together in low-carbon iron crucibles under pure argon. Alloys containing up to 20% of thorium are bright-rose coloured and all are soft and plastic. The phase-diagram given in Fig. 23 has been prepared from thermal analysis and times of arrest on solidification. The m.p. of sodium, 97°C., is first lowered by addition of thorium to a eutectic point at 92°C. and 25% by weight of thorium. The compound Na_4Th is formed by a peritectic reaction at 121°C.[390]

The solubility of iron in sodium between 225° and 500°C. is given by: $\log S_T = 1{\cdot}8266 - 558{\cdot}5/T$, where S_T is the solubility in p.p.m. by weight at T°K. or by $10^4 \times W = -1{\cdot}1 + 0{\cdot}02767t$, where W = wt.-% and t = °C. The solubility has also been given as $10^4 \times W = 1{\cdot}0 + 0{\cdot}0220t$. Both equations are based on wet chemical analysis. Radiochemical determinations give lower results and as yet no satisfactory explanation for the discrepancy has been found.[1]

According to Zieler[391] sodium is unsuitable as a deoxidizing agent because satisfactory steel ingots cannot be cast.

In the development of high-strength cast iron, *i.e.* in the reduction of graphite in cast iron to particles of extreme fineness, it has been found that the addition of sodium or sodium alloys brings about this result but that the improvement is insufficient to compensate for the difficulties encountered in adding sodium,[392] but see also[393-396].

The solubility of nickel in sodium is given by the expression: $10^4 \times W = -0{\cdot}085 + 0{\cdot}0358t$ where W = wt.-% and t = °C.[1]

The m.p. of sodium is lowered 0·4°C. by the presence of 2·8% of palladium.[1]

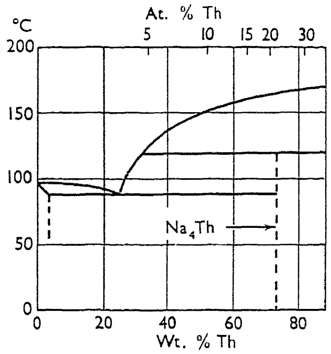

FIG. 23. EQUILIBRIUM DIAGRAM Na–Th

Only 'trace' amounts of platinum dissolve in liquid sodium although sodium vapour has a corrosive effect on platinum. The addition of up to 1·5 wt.-% of platinum does not affect the m.p. of sodium.[1]

Cerium is slightly miscible in liquid sodium.[1]

Fig. 24 shows the solubilities of metals in liquid sodium.[1]

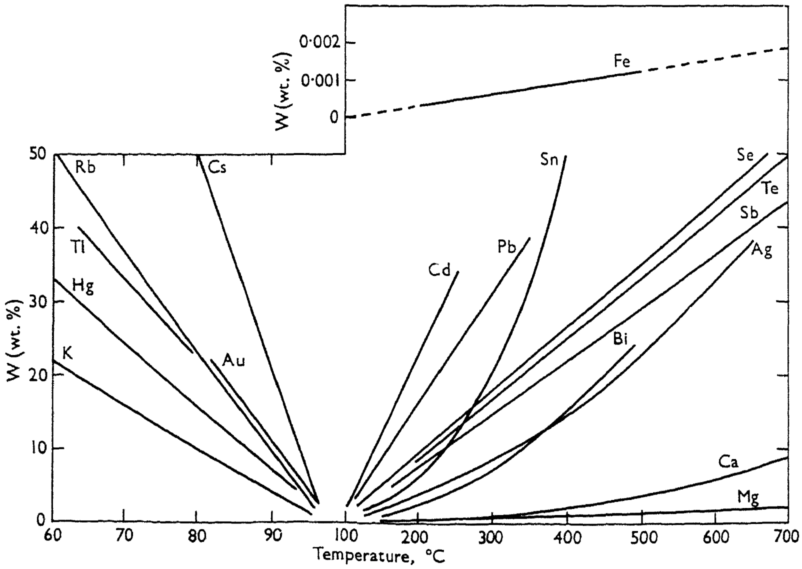

FIG. 24. SOLUBILITIES OF METALS IN LIQUID SODIUM

Halla and Herdy[397] have measured the e.m.f. of liquid sodium against liquid sodium-mercury-lead alloys at 350° and 400°C. and calculated the activities of sodium in alloys of several mercury:lead ratios. The solutions are shown to be non-ideal. The activities of mercury have been calculated from vapour-pressure measurements at 400°C. for mixtures of varying atomic ratios of sodium:lead. Free energies and heats of mixing are given. Kubaschewski and Catterall[38] consider that a temperature interval of 50°C. is rather small for the derivation of reliable entropy values and suggest that the values given by Halla and Herdy should be disregarded. The last two authors have interpolated compositions for equal values of $\Delta\overline{G}_{Na}$ *i.e.* partial free energy (or change in free energy when 1g.-atom of sodium is assimilated by a theoretically infinite amount of an alloy of constant composition N_{Na}) for 400°C. and these are given in Table LIII.

TABLE LIII. PARTIAL FREE ENERGY OF SODIUM, $\Delta\overline{G}_{Na}$, IN Na-Hg-Pb AT 400°C.

$\Delta\overline{G}_{Na}$ = −2,000 (g.-cal.)		−4,000 (g.-cal.)		−6,000 (g.-cal,)		−8,000 (g.-cal.)	
N_{Na}	N_{Hg}	N_{Na}	N_{Hg}	N_{Na}	N_{Hg}	N_{Na}	N_{Hg}
0·708	0	0·548	0	0·415	0	0·281	0
0·676	0·065	0·536	0·093	0·404	0·119	0·286	0·143
0·674	0·109	0·516	0·161	0·398	0·201	0·29	0·237
0·642	0·179	0·50	0·25	0·388	0·306	0·293	0·353
0·612	0·259	0·48	0·347	0·372	0·419	0·301	0·466
0·598	0·321	0·47	0·424	0·368	0·505	0·306	0·555

$\Delta\overline{G}_{Na}$ = −10,000 (g.-cal.)		−12,000 (g.-cal.)		−14,000 (g.-cal.)	
N_{Na}	N_{Hg}	N_{Na}	N_{Hg}	N_{Na}	N_{Hg}
0·15	0	(0·025)	0	–	–
0·178	0·164	0·072	0·185	–	–
0·20	0·267	0·112	0·296	0·044	0·319
0·212	0·394	0·145	0·428	0·07	0·465
0·23	0·513	0·160	0·559	0·098	0·60
0·239	0·609	0·174	0·661	0·118	0·706

$\Delta\overline{G}_{Hg}$ = −500 (g.-cal.)		−1,000 (g.-cal.)		−2,000 (g.-cal.)		−2,500 (g.-cal.)	
N_{Hg}	N_{Pb}	N_{Hg}	N_{Pb}	N_{Hg}	N_{Pb}	N_{Hg}	N_{Pb}
0·52	0·48	0·30	0·70	–	–	–	–
0·796	0·163	0·625	0·30	0·302	0·558	0·19	0·648
0·82	0·12	0·698	0·201	0·404	0·397	0·29	0·473
0·838	0·081	0·74	0·13	0·478	0·261	0·38	0·31
0·858	0·047	0·76	0·08	0·58	0·14	0·512	0·163
0·862	0·027	0·78	0·044	0·646	0·071	0·598	0·080
0·87	0	0·80	0	0·712	0	0·672	0

Jollivet[398] has studied ternary systems rich in lead and containing sodium and antimony or sodium and arsenic. The solid phase which separates out near the eutectic when the liquid phase contains more than 1·7% of antimony in the lead-antimony-sodium system has the composition shown by the formula Na_3Sb. At lower concentrations of antimony, the solid phase is NaSb. Between 0·1 and 0·5% of antimony and at the eutectic temperature, 325°C., the atomic concentrations of antimony and sodium are given by the equation:-

$$\log(Sb) + 3\log(Na) = -7{\cdot}37.$$

Between 2 and 2·5% of antimony and at a temperature of 310°C. the relation is:-

$$\log(\mathrm{Sb}) + \log(\mathrm{Na}) = -3{\cdot}49.$$

At the binary eutectic between 1 and 0·02% of arsenic and at about 325°C., the solid phase separating out from the lead–arsenic–sodium system is the compound NaAs. The atomic concentrations in the liquid phase are given by:-

$$\log(\mathrm{As}) + \log(\mathrm{Na}) = -5{\cdot}17.$$

In the lead–antimony–tin–sodium system, mixtures containing 0·02–0·35% Na, 0·1–0·5% Sn, 0·01–0·7% Sb have been studied. The solid phase near the eutectic has the composition given by the formula NaSnSb and the isotherm of the liquid at 355°C. is given by:-

$$\log(\mathrm{Sb}) + \log(\mathrm{Sn}) + \log(\mathrm{Na}) = -7{\cdot}91.$$

Thermal investigation of the ternary system, magnesium–sodium–lead carried out by Calingaert and others[399] show the presence of a peritectic type of compound, MgNaPb, and the compound, $Mg_4Na_4Pb_3$.

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SECTION XXVII

SODIUM HYDRIDE

By A.B. LITTLEWOOD

Occurrence, Preparation and Purification

Although sodium hydride is much too reactive to occur naturally on earth, it has been suggested that it is present in certain stars and comets as a dilute vapour, where its presence would serve to explain the observed ultraviolet spectrum.[1]

The preparation of sodium hydride by direct combination of sodium and hydrogen has been studied by many workers, and the process is carried out commercially. At too high a temperature, there is incomplete reaction on account of dissociation (see below); at too low a temperature, the reaction is extremely slow,[2] though it starts below the melting point of sodium.[2,3] The rate of reaction has been studied, and it is found that the logarithm of the rate of formation of hydride is a linear function of temperature both below and above the melting point of sodium, though there is a discontinuity at the melting point. At 100°C., 0·00061c.c. of hydrogen combine per hour per sq. cm. of sodium surface.[3] Most workers find that the most satisfactory temperature for the reaction is between 200 and 300°C.

The speed of the formation reaction is reduced by the formation of a layer of hydride on the surface of the metal, and all satisfactory preparations use the sodium in a finely divided form or as vapour. In one laboratory preparation, sodium is distilled from a metal container into a glass vessel containing hydrogen, and the hydride condenses in cooler parts of the vessel. Up to 1g. per hour was prepared in this way.[3,4] In another laboratory preparation, sodium metal (50g.) is suspended in 500c.c. of stirred hexane, heptane, or octane at 299°C. in an autoclave, and caused to react with hydrogen under pressure.[5] Manufacturing methods for sodium hydride are the subject of a number of patents.[6] In some of these, liquid sodium is sprayed into an atmosphere of hydrogen at 180°-250°C. In other systems, the sodium is distributed on an inert solid carrier, which may be already formed sodium hydride or another solid diluent, such as sodium chloride, charcoal, etc. In another patent,[7] the use of organic catalysts for the reaction is described. The reaction is catalysed by aliphatic acids having more than eight carbon atoms, or their salts, e.g. 2% by weight of magnesium stearate, or by certain hydrocarbons such as *p*-cymene, but excluding aliphatic hydrocarbons.[7]

Sodium hydride may also be obtained by treating molten sodamide with hydrogen at a temperature not exceeding 200°C. The resulting hydride can then be extracted with liquid ammonia.[8] It is also formed by reducing other sodium compounds with hydrogen, for example the oxide or hydroxide;[9] in these cases sodium metal is presumably an intermediate.

Pure sodium hydride can be prepared from material of commercial grade by carefully controlled distillation *in vacuo* from an iron crucible contained in an all glass apparatus. The 'distillation' involves the decomposition of the hydride into its elements, followed by their recombination in cooler parts of the apparatus, and therefore the pressure rises during the distillation owing to the hydrogen formed.[10] The distillation must not be carried out too fast, or sodium metal may contaminate the product.

Solid sodium hydride should not be heated in direct contact with glass, for sodium produced by dissociation may exchange with calcium in the glass to give calcium metal, which forms a hydride more stable than sodium hydride.[21] The net result may be the formation of calcium hydride as a contaminant. When sodium hydride is heated in a glass apparatus, it should be contained in an iron or other inert metal container.

Sodium deuteride can be prepared in the same way as the hydride,[4,11] but the absorption of deuterium is slower than that of hydrogen.[11]

Properties

Sodium hydride is a white crystalline solid with a cubic sodium chloride type lattice,[12,13] having d 1·396 ± 0·005 as determined by a suspension method,[10] or 1·38 ± 0·04 determined pycnometrically.[14] The lattice constant is 4·880A.[14a] No melting point has been reported, and it appears that the hydride is fully dissociated before it melts.

Sodium hydride is a very reactive substance the use of which is attended by some hazard. Although not spontaneously inflammable in the ordinary way, it may sometimes ignite spontaneously.[10] Usually it will inflame on slight heating in air. Sufficient heat may be provided by a spot of water touching the powdered hydride, and thus if the hydride is moistened, it may inflame. It is hydrolysed by water instantaneously to give hydrogen and sodium oxide, hydroxide, or sodium hydroxide solution according to the ammount of water. The heat of solution for the reaction:-

$$\mathrm{NaH\ (s) + H_2O\ (l) \rightarrow NaOH\ (inf.\ dil.\ soln.) + H_2\ (g)}$$

is given as 31·57 ± 0·15 kg.-cal./mole[10] or 30·63 ± 0·23 kg.-cal./mole.[15]

On heating, it decomposes reversibly into its elements. In this respect it is more stable than KH, but less stable than lithium hydride. The lattice energy of sodium hydride has been calculated to be 189 kg.-cal./mole,[16] in comparison with values of 217 for lithium hydride and 166 kg.-cal./mole for potassium hydride. The binding energy of gaseous sodium hydride has been shown to be 150 kg.-cal./mole, both by calculation and experimentally.[17] The pressure of hydrogen above heated sodium hydride has been measured by many authors. A selection of such values is given in Table I. The results can conveniently be given by the two-parameter Antoine equation, $\log p_{H_2}$(mm.) $= A/T + B$; values for A and B determined by different authors are given in Table II.

TABLE I. - DISSOCIATION PRESSURES OF SODIUM HYDRIDE

Temp. °C.	p_{H_2} (NaH) mm.Hg	Ref.	Temp. °C.	p_{D_2} (NaD) mm.Hg	Ref.
285	4·5	19	271·2	2·8	21
288·5	6·2	20	301·3	14·8	21
306	13·2	20	321·5	39·1	21
331	36	20	349·0	124·3	21
347	68	20	356·7	157·3	21
350	51	19			
360	75	18, 19			
382	233·5	20			
390	261	18, 19			
415	620	20			
425	585	19			

Refs. p. 626

TABLE II.- ANTOINE CONSTANTS FOR THE DISSOCIATION OF SODIUM HYDRIDE AND SODIUM DEUTERIDE

NaH			NaD		
A	B	Ref.	A	B	Ref.
-6100	11·66	3, 20	-7313	13·80	4
-6318·41	11·9250	21	-6915·00	13·1994	21
-5070	10·49	(a) 22			
-5958	11·47	(b) 22			
-6222	12·70	(c) 22			

The heat of formation of solid sodium hydride has been determined from the dissociation pressure data given above and by subtracting the heat of hydrolysis of sodium metal from that of sodium hydride. Table III gives values for the heat of formation, indicating the method used.

TABLE III.- HEATS OF FORMATION OF SODIUM HYDRIDE AND SODIUM DEUTERIDE

NaH			NaD		
Value g.-cal./mole	Method	Ref.	Value g.-cal./mole	Method	Ref.
13940	D	20,3	21500 (285°C.)	D	4
14440	D	21	20900 (341°C.)	D	4
12800	C	10	15800	D	21
13700	C	23			
13600	C	15			
11610	D	(a) 22			
13590	D	(b) 22			
14250	D	(c) 22			

C = by calorimetry
D = by dissociation pressure

It is reported that sodium hydride is insoluble in sodium metal and vice-versa up to temperatures of 150°C.[3] This observation is supported by the fact that mixtures of sodium hydride and sodium metal have the same melting point as sodium metal.[24] At higher temperatures, however, the influence of sodium on the hydrogen pressure of sodium hydride suggests mutual solubility.[3,22] This is most clearly shown in the results (ref. 22) given in Tables II and III, which were obtained between 500°C. and 600°C. The results marked (a) were obtained from a sample of pure sodium hydride; those marked (b) from samples containing anything between 30 and 80% of sodium hydride and those marked (c) from those containing 10% sodium hydride. The vapour pressure is independent of composition between 30 and 80% NaH, but outside these limits changes markedly with composition. This indicates that within the 30–80% range there is a two phase region consisting of sodium saturated with hydride and hydride saturated with sodium, but that outside these limits there is only a one phase system consisting of an unsaturated solution of the minor component in the major. A study of the results in Table III suggests that the data of other workers apply to the saturated solution of sodium hydride. This would inevitably be so if an appreciable amount of hydride were used up in providing the hydrogen pressure for measurement.

The dissociation pressure of sodium deuteride is always greater than that of the hydride, so that the deuteride is considerably less stable. Table IV gives the difference in the dissociation pressures as measured by a differential method.[4,25] Table I also gives dissociation pressures of sodium deuteride,[21] and Tables II and III contain Antoine constants and heats of

TABLE IV. - DIFFERENCES IN DISSOCIATION PRESSURE BETWEEN SODIUM HYDRIDE AND SODIUM DEUTERIDE

Temp. °C.	$P_{NaD}-P_{NaH}$ (mm.Hg)
260	0·1
270	0·5
280	1·9
290	3·3
300	4·1
310	7·7
320	10·8
330	19·0
340	28·3
350	42·8

formation for the compound. Since dissociation pressures of the hydride are only of the order of half those of the deuteride, dissociation of the mixture has been suggested as a method of separating the isotopes.[4]

Sodium hydride is soluble in fused metal halides, for example, the eutectic mixture of potassium and lithium chloride.[26] Solutions of sodium hydride in solid sodium chloride have been suggested as providing a more stable and less hazardous form of the hydride for use in the laboratory.[27]

Sodium hydride reacts with amino-, imino-, amido-, or imido- compounds to replace the hydrogen by sodium, with evolution of hydrogen. A purely inorganic example is provided by the reaction with ammonia, which is reversible:-[28]

$$NaH + NH_3 \rightleftharpoons NaNH_2 + H_2$$

This reaction is, however, complicated by decomposition of the sodium amide at the temperature used.[28] Aniline gives C_6H_5NHNa on warming with sodium hydride, and other organic compounds containing the above mentioned groups react similarly.[29]

With boron trifluoride at -70°C., sodium hydride gives $Na(HBF_3)$, which reacts further with sodium hydride at 200°C. to give $Na(H_2BF_2)$.[30] The reaction does not continue, however, to give sodium borohydride, $NaBH_4$. Excess sodium hydride reacts with boron trifluoride diethyl etherate, BF_3,Et_2O, to give diborane,[31] although lithium hydride is also used in this important reaction. Unlike lithium hydride, sodium hydride does not react with diborane to give sodium borohydride.[31] With borate esters, $B(OR)_3$ (R = Me, Et, Bu), sodium hydride gives compounds of the type $NaBH(OR)_3$, and with ethylboron, Et_3B, it gives $NaNHEt_3$. Sodium hydride and trimethylborate at 225-275°C. give a good yield of sodium borohydride.[31] Ethyl aluminate and sodium hydride give the compound $NaAlH(OEt)_3$, as with boron, in ethereal solution using lithium aluminium hydride as a catalyst.[32]

The hydrolysis of sodium hydride by water gives molecular hydrogen as an initial product instead of first giving hydrogen atoms. This is suggested by the fact that sodium hydride does not decolourise an aqueous solution of the dye safranine T.[33] It does not follow that, because sodium hydride is a combination of two reducing agents, it is *a fortiori* a stronger reducing agent than either; this is not so, as is illustrated by the example below.

Sodium hydride may be used in place of sodium as a condensing agent in Claisen-type condensations, the progress of the reaction being conveniently followed by the evolution of hydrogen. Examples are the Stobbe condensation,[34] amino-acid synthesis,[35] ketone synthesis,[36] or ester synthesis.[37] In this connection, sodium hydride is particularly useful in that, unlike sodium, it does not reduce carbonyl groups. Finely powdered sodium hydride has been used as a catalyst for ester-ester interchange, using 0·05%-0·5% in the anhydrous ester mixture at temperatures of 0-120°C. Examples are the interconversion of glycerol esters amongst themselves, or with other esters, or with fatty acids,[38] or glycerol with alkyl terephthalates.[39] Reactions in which sodium hydride is used in liquid suspension require the hydride to be finely divided, and a ball mill for grinding and simultaneous reaction has been described.[40] Sodium hydride acts as a catalyst in the hydrogenation of hydrocarbons such as anthracene, naphthalene etc. In its presence anthracene may be hydrogenated at 300° instead of at 470-500°C. The action appears to be confined to those parts of the organic molecule with which the sodium can combine, so that it is not catalytic in the reduction, for example, of phenyl groups. Reduction of naphthalene gives tetralin, not decalin.[41-43] Sodium hydride may also be used as a polymerisation agent for butadiene,[44,45] and for carbon monoxide-ethylene copolymers.[46]

A recent commercial application of sodium hydride is in the descaling of both ferrous and non-ferrous metals (the Dupont process). In general, the metal object to be descaled is dipped in a bath of fused sodium hydroxide at about 350°-370°C. in which is dissolved about 2% by weight of sodium hydride, for a period between a few seconds and 30 minutes, depending on the scale thickness and whether or not the metal has been pre-heated. The metal, with the reduced scale still on its surface, is then plunged into cold water, when the violence of the steam formation blasts the reduced scale off the surface of the metal. The method can be used for any metal not attacked by sodium hydroxide at the temperature required; iron, nickel and cobalt scales are reduced to metal, chromium scale is reduced to a lower oxide. The sodium hydride concentration is not critical, and the bath operates well down to 1·5% concentration. The sodium hydride is generated in situ by reaction of the elements. No hydrogen embrittlement occurs.[47] The method has been successfully used with titanium,[48,49] but hydrogen is liable to be absorbed by the metal if this is immersed for too long.[50]

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SECTION XXVIII

SODIUM OXIDES

By G. SCHOLES

Sodium forms three oxides, sodium monoxide, Na_2O, sodium peroxide, Na_2O_2 and sodium superoxide, NaO_2. Earlier workers (Mellor,II,487) suggested the existence of a sesquioxide, Na_2O_3, but the data do not substantiate this claim. In addition to the above named oxides, sodium also forms an ozonate, NaO_3.

SODIUM MONOXIDE

Very pure samples of sodium monoxide can be prepared by heating sodium azide with sodium nitrate,[1] the reaction being: $5NaN_3 + NaNO_3 \rightarrow 3Na_2O + 8N_2$. This reaction is carried out in a nickel boat in a hard glass tube, the boat being coated with azide to prevent attack, and sodium nitrate being preferred to sodium nitrite because of its higher melting point. The reaction is conducted in a vacuum, the temperature being slowly raised to 350°. The time required is 3–5 hr. but the sodium oxide so obtained is claimed to be 100% pure. Samples of high purity have also been prepared by thermal decomposition of sodium peroxide in a vacuum and by the reduction of sodium peroxide or sodium superoxide with molten sodium at about 500°.[2]

Sodium monoxide is an intermediate in the manufacture of sodium peroxide from molten sodium and dry air or oxygen.[3-5] The reaction is carried out at 180–220° in a rotary-tube furnace and in the presence of fairly large amounts of previously formed monoxide. The conditions can be adjusted so that external heating of the furnace is unnecessary. Sodium monoxide produced in this way may contain absorbed sodium (up to 0·5%) but can be purified by heating to at least 250° in the presence of small quantities of oxygen.[6,7]

Sodium monoxide may also be prepared from a fused mixture of sodium and sodium hydroxide.[8] Hydrogen is added until absorption is complete and the mixture is then maintained at 400–600° in a stream of inert gas until the evolution of hydrogen ceases.

Other methods of preparation involve a controlled reaction between sodium and sodium peroxide[9] and the oxidation of sodium amalgam.[10]

Sodium monoxide melts at 920°,[2,11] begins to vaporize at 1350° and boils above 1600°.[11] A sublimation point of 1275° (at 600 mm. pressure) has also been reported.[12]

The equilibrium vapour pressures over solid sodium monoxide have been determined by the Knudsen effusion method over the temperature range 918–1467°K.[2,13] In agreement with theoretical predictions,[14] these data show that the vapour consists predominantly of sodium atoms and oxygen molecules, with monoxide molecules much less important than the elements under neutral conditions. Sodium vapour and oxygen gas do not react with each other unless at high enough pressure to deposit the monoxide. These vapour pressure experiments led to a limit for D_0, the dissociation energy of the gaseous atoms at 0°K., of $D_0 \leqslant 144$ kg.-cal./mole.

Heat contents of sodium monoxide above 298·16°K. at 100° intervals to

1100°K. have been estimated,[15] leading to the following specific heat equation:-

$$C_p = 15{\cdot}9 + 0{\cdot}0054T.$$

Some thermodynamic properties of the oxide have been discussed by Brewer[16] and the following values given:-

$$\Delta F_{298\cdot16} = -90 \text{ kg.-cal./mole}$$

$$\Delta H_{298\cdot16} = -99{\cdot}4 \pm 1 \text{ kg.-cal./mole}^{17,18}$$

$$\Delta S_{298\cdot16} = -31{\cdot}9 \text{ e.u./mole.}^{19}$$

The entropy of $Na_2O(s)$ at 298·16°K. has been estimated as 17·4 ± 0·8 e.u./mole.[20] Estimates have also been reported[13] for the heat of fusion (10 kg.-cal./mole), entropy of fusion (8·4 e.u./mole) and the heat capacity of $Na_2O(l)$ (24 kg.-cal./deg.mole). The heat of solution in water is 55·97 kg.-cal./mole.[17]

The contraction constant, defined as the ratio of molecular volume of sodium monoxide to the sum of the atomic volumes of the component elements, is 0·44; this value corresponds to an ionic lattice.[21] The molar susceptibility has been calculated to be $-19{\cdot}8 \times 10^{-6}$ c.g.s. units.[22] Using the principle of additive polarizabilities of the ions the dielectric constant has been estimated as 4·65; the estimated molecular volume is 42·74.[23] The atomic refraction of sodium in sodium monoxide has a value of 0·90.[24] The decomposition voltage of the fused oxide is in the range 1·0–1·2 V.[25]

The lattice structure of sodium monoxide has been investigated by *X*-ray methods and found to be of the fluorite type, with four sodium atoms and four oxygen atoms in the unit cell; the density was calculated to be 2·39.[1]

The solubility of sodium monoxide in liquid sodium over the range 115–495° can be expressed by the relationship:[26] $\log y = 1{\cdot}266 - (1816/T)$, where y is the solubility (in wt.-% of oxygen in sodium) and T is the temperature in °K.

Dry chlorine will not react with sodium monoxide but in the presence of moisture sodium peroxide is formed: $2Na_2O + Cl_2 \rightarrow 2NaCl + Na_2O_2$.[1] With nitric oxide a vigorous reaction sets in at temperatures above 100° leading to the formation of sodium nitrite and sodium hyponitrite.[1] Recent work[27] on this system has shown that sodium nitrite and nitrogen are formed according to the equation:- $Na_2O + 3NO \rightarrow 2NaNO_2 + \frac{1}{2}N_2$. Sodium monoxide reacts with acetylene to form sodium carbide.[28]

Reactions with iron, tungsten, molybdenum, cobalt and nickel yield complex metal oxide–sodium monoxide compounds with evolution of sodium vapour.[11] The reaction begins at 550° for iron, 500° for tungsten, 600° for molybdenum and above 1000° for both cobalt and nickel. When aluminium is heated with the alkali metal oxide, sodium aluminate is formed.[11] At high temperatures (around 500°C.) sodium monoxide attacks several types of steel, particularly carbon steels and low alloy steels.[29]

On heating glass melts directly with a reducing flame, measurable amounts of alkali are lost and this has been attributed to reduction of sodium monoxide to sodium by the carbon monoxide of the flame.[30]

The decomposition of orthophosphates of the apatite types on heating with the oxide at 1200° has been examined.[31] The following reaction occurs:- $Ca_{10}F_2(PO_4)_6 + 4Na_2O \rightarrow 6CaNaPO_4 + 4CaO + 2NaF$. This, in the presence of excess of sodium monoxide, can be followed by the reaction: $6CaNaPO_4 + 6Na_2O \rightarrow 6Na_3PO_4 + 6CaO$. The activation energy of the catalytic decomposition of ozone by sodium monoxide has been given as 4·1 kg.-cal./mole.[32]

Thermal relations in the systems Na_2O–Na_2SO_4 and Na_2O–Na_2S have been investigated by melting–cooling behaviour.[33] These systems show single eutectics at 550° and 682° respectively. Limited solubility in the solid state was exhibited. The system $Na-H_2-NaOH-Na_2O$ has been investigated at various temperatures[34] and the composition of the phases determined by measurements of the hydrogen pressure. The reduction of sodium monoxide to sodium hydride by hydrogen in this system begins at 110°. In the system Na_2O-NaO_2[35] there is a sequence of continuous compounds, varying from Na_2O_4 to $Na_2O_{3\cdot 60}$.

A method for the determination of sodium monoxide in sodium has been developed by Pepkovitz and Judd.[36] The oxide is quantitatively separated by treating the mixture with mercury in a special apparatus (removing the sodium) and then dissolved in water and titrated. Modifications of the method have been described.[37,38]

Although used in the greatest quantities for the production of sodium peroxide, sodium monoxide has other minor uses e.g. in the glossing of corundum and spinel,[39] as a slag-former in ilmenite refining[40] and in the formation of titanium concentrates from titaniferous ores.[41]

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SODIUM PEROXIDE

Sodium peroxide is formed by the rapid oxidation of metallic sodium dissolved in liquid ammonia[1] and by the oxidation of sodium amalgam.[2,3] The latter reaction is catalyzed by K_2O_4.[3] The peroxide is a product of the reaction of oxygen with the disodium compound of anthrahydroquinone dissolved in benzene[4] and also of oxygen with a solution of sodium ethoxide and hydrazobenzene or anthrahydroquinone in ethanol.[5] Moist chlorine will oxidize sodium monoxide to sodium peroxide.[6]

Commercially, sodium peroxide is produced by the oxidation of sodium monoxide by oxygen. In the process described by Carveth,[7,8] sodium monoxide, mixed with up to 10% of sodium metal, reacts with oxygen in the temperature range 200–350°, the reaction being carried out in a rotary steel burner. In another process[9] metallic sodium is first burned in an iron rotary tube in a current of hot air at 200–250° and the reoxidation is carried out in nickel-lined rotary tubes through which pure oxygen is flowing in countercurrent to the monoxide feed. The sodium monoxide oxidation has also been carried out in a pressure chamber at 350–490°.[10] A process has been described[11-13] in which (*a*) sodium and sodium peroxide are allowed to react in an oxygen-free atmosphere at 260–400° to form the monoxide and then (*b*) the monoxide is oxidized further in an oxygen-containing atmosphere at 400–430°. Part of the sodium peroxide is recycled and part is withdrawn.

The peroxide can also be prepared directly from sodium. In one method[14] the metal vapour is burned in an excess of oxygen or air, an inert gas being used to carry the vapour and a Cottrell precipitator or entrainment trap being used to collect the finely-divided product. In another method[15] a thin film of liquid sodium is poured over the surface of a carrier heated to 450–575° and the whole is rotated in a stream of air. Commercial sodium peroxide usually has a minimum purity of 96%.

The chief uses of sodium peroxide depend upon the bleaching properties of its aqueous solutions. It has been used successfully for the bleaching of textiles[16-18] e.g. wool, cotton, linen, rayon and jute. Recent applications are in the bleaching of wood pulps e.g. groundwood,[19-22] sulphite pulps[23-25] and sulphate pulps;[26,27] the use of sodium peroxide in the pulp industry has been reviewed.[28-31] The peroxide is also used for the bleaching and de-inking of waste papers.[32-34] Stabilized solutions can be employed for the preparation of compounds such as alkaline earth peroxides, diacyl peroxides or perborates.[35] The solid material is used in respirators,[36-39] in the cleaning of stainless steels,[40,41] in fluxes employed for the thermochemical cutting of steels,[42] in analytical fusion techniques[43-46,47] and as an aid in the recovery of metals from ores.[48]

According to Blumenthal[49,50] sodium peroxide melts at 460° and dissociates at 657°. Bunzel and Kohlmeyer[51] observed a melting point of 675°. More recently it has been reported[52,53] that the peroxide begins to decompose slowly at 280°, melts at 510° and at 510–545° decomposes to sodium monoxide and oxygen.

The yellowish colour of commercial sodium peroxide has been occasionally attributed to impurities (e.g. iron) but there is no doubt that the colour is essentially due to the presence of sodium superoxide (NaO_2): it has been shown that some samples can contain up to 10% of the superoxide.[54]

Sodium peroxide crystals are hexagonal and crystal rotation patterns and powder patterns yield the repeat distances,[55] $a = 6{\cdot}22 \pm 0{\cdot}01$ A. and $c = 4{\cdot}47 \pm 0{\cdot}01$ A. Density measurements on the peroxide (2·2 to 2·8 g./c.c.) favour a unit cell containing three Na_2O_2 units, giving a calculated density of 2·60 g./c.c. In this structure the peroxide ions lie parallel to the *c*-direction, one at the corner and three within the unit cell, and each is in contact with nine sodium ions, three about the middle and three about each end. A sodium ion of radius 0·98 A. and a peroxide ion regarded as a cylinder of radius 1·29 A. and length 1·49 A. with caps of radius 1·29 A. are consistent with this structure and with other crystallographic data.

The heat of dissociation of sodium peroxide is 37·7 kg.-cal.[56] The dissociation pressure has been measured over the temperature range 580–650°, leading to the equation:-[50]

$$\log p\ (\text{mm.}) = 17{\cdot}19 - (60{,}340/4{\cdot}571T).$$

Heat capacity measurements over the low temperature range 50–298°K. have been carried out[57] (see Table I) and from these data the entropy at 298·16°K. has been evaluated as $S^{\circ}_{298\cdot16} = 22{\cdot}6 \pm 0{\cdot}3$ g.-cal./deg.mole. Values for the heat capacities at somewhat higher temperatures *viz.* from 292–373°K. are also available;[58] the average value over this range has been given as 21·46 g.-cal./deg.mole.

TABLE I.- HEAT CAPACITIES OF SODIUM PEROXIDE AT VARIOUS TEMPERATURES[57]

Temp. °K.	Heat capacity, C_p (g.-cal./deg.mole)
52·31	2·85
106·35	10·52
154·62	15·29
205·61	18·28
255·27	20·17
296·22	21·26

Gilles and Margrave[59] have studied the reaction $Na_2O_2(s) + H_2O(l) \rightarrow 2NaOH(l) + \frac{1}{2}O_2(g)$ catalyzed by manganese dioxide and have obtained for the solution reaction $\Delta H = -34 \pm 0{\cdot}3$ kg.-cal. From this they have calculated that the heat of formation of sodium peroxide at 298·16°K. is $-122{\cdot}1 \pm 1{\cdot}2$ kg.-cal./mole. Recalculation by these authors of the data of de Forcand (Mellor, II, 487) and of Roth and Kaule[60] leads to values of −119·3 and −121·2 kg.-cal./mole respectively for the heat of formation of the peroxide.

The molar susceptibility measured by the Curie method and corrected for the presence of ferromagnetic impurities[61] leads to a value $\chi_M = -28{\cdot}1 \times 10^{-6}$ c.g.s. units. This result has been taken as supporting the structural formula of the peroxide as Na–O–O–Na.

Sodium peroxide forms a series of hydrates (Mellor, II, 489). If the anhydrous peroxide is exposed to moist carbon dioxide-free air at room temperature, large, tabular, white crystals of the octahydrate, $Na_2O_2{,}8H_2O$, are formed.[62] This hydrate can also be obtained from solutions of sodium hydroxide which have been treated with hydrogen peroxide.[63,64] The octahydrate is produced commercially by hydrating the peroxide spread as thin layers in a closed chamber at the bottom of which lies a layer of water heated to about 40° by steam.[65] The octahydrate crystals belong to the monoclinic system.[62] The body-centred unit cell contains four molecules, and *X*-ray rotation photographs give the identity periods a = 13·49 A., b = 6·45 A., c = 11·49 A. and β = 110° 31′. The space group is either C_2^{6h} or C_s^4. The density at 25° is 1·61.

Methods for the preparation of other sodium peroxide hydrates have been described.[66,67] The peroxide or the octahydrate is kept in a closed vessel containing water vapour at the required partial pressure; $Na_2O_2,2H_2O$ and Na_2O_2,H_2O have been prepared in this way.

The hydrate $Na_2O_2,2H_2O_2,4H_2O$ (which can be regarded as a hydroperoxide $NaO_2H,0{\cdot}5H_2O_2,2H_2O$) as well as the octahydrate, have been identified by solubility methods in the system $NaOH$–H_2O–H_2O_2 and their thermal stabilities and dehydration studied.[66]

Carbon dioxide reacts with sodium peroxide to form sodium carbonate ($Na_2O_2 + CO_2 \rightarrow Na_2CO_3 + \frac{1}{2}O_2$) but this proceeds rapidly only in the presence of water bound to the peroxide.[68] It has been shown, using preparations of Na_2O_2,nH_2O, where n varies from 0 to 8, that the reaction is maximal when n = 2.

The peroxide reacts with oxygen at high temperatures and pressures to form sodium superoxide.[69] Hydrogen atoms generated by an electric discharge reduce the peroxide to the hydroxide.[70]

The use of sodium peroxide in analytical fusion techniques[43-46] has stimulated some interest in the action of this substance on metals. It has been long known that there is a vigorous reaction between sodium peroxide and aluminium powder, which can be initiated by moistening.[71,72] Explosive reaction has also been observed with magnesium.[72] At comparatively low temperatures (< 240°) it has been found that all metals except nickel are attacked;[51] the reaction with powdered nickel begins only at temperatures in the range 500–780°. In a typical fusion experiment[46] it has been observed that, using 1 part of the sheet metal to 30 parts of peroxide, titanium dissolves in 10 min. and vanadium in 2 hr., but that zirconium lost only 4% of its weight as a hard grey film. Crucibles made from pure zirconium are, in fact, particularly resistant to attack by sodium peroxide.[47] In the main, however, iron, silver or nickel crucibles have been used for peroxide fusions. Platinum has been avoided on account of severe attack although in this respect it has been shown more recently[45] that, provided the temperature is kept below 540°, sodium peroxide decompositions of the most resistant minerals can be made in platinum vessels without their losing weight. The inertness of zirconium has been applied in the construction of mixing paddles and other moving parts used in the methods of manufacture of sodium monoxide from sodium peroxide and sodium. It has been reported[73] that paddles made of or coated with zirconium lasted at least four times longer than paddles made from nickel steel, iron, titanium or various other materials in the operating range 260–425°.

Sodium peroxide reacts with many oxides on heating. From infra-red examination it has been established that the following compounds are formed:[74]

Na_4TiO_4 from TiO_2

Na_2UO_4 from UO_3, U_3O_8, U_3O_7 or UO_2

Na_4GeO_4 (and in part Na_2GeO_3) from GeO_2

$NaSbO_3$ from Sb_2O_5 (but not from Sb_2O_3)

Na_4SiO_4 from SiO_2.[75,76]

On heating mixtures of sodium peroxide and aluminium oxide to 300° no polymerized aluminates were detected.[77] With V_2O_3 and an equimolar amount of peroxide, $NaVO_3$ was formed under these same conditions. With one mole of V_2O_5 and three moles of peroxide the reaction product below 300° was Na_3VO_3 but above 670° was a mixture of meta- and ortho-vanadates. The reactions between sodium peroxide and several oxides of the transition elements have been studied;[78] with CrO_3, the formation of Na_2O,CrO_3 was not complete, even in the presence of excess peroxide.

Sodium peroxide is one of the most powerful decomposing agents for minerals. The following equations have been used to calculate the theoretical amounts of oxygen evolved on treatment of various minerals and a fairly good agreement has been observed between the actual and the theoretical evolutions.[45]

Quartz: $SiO_2 + 2Na_2O_2 \rightarrow Na_4SiO_4 + O_2$

Rhodonite: $2MnSiO_3 + 6Na_2O_2 \rightarrow 2Na_4SiO_4 + 2Na_2MnO_4 + O_2$

Rutile: $TiO_2 + 2Na_2O_2 \rightarrow Na_4TiO_4 + O_2$

Beryl: $3BeO,Al_2O_3,6SiO_2 + 16Na_2O_2 \rightarrow 6Na_4SiO_4 + 3Na_2BeO_2 + 2NaAlO_2 + 8O_2$

Chromite: $2(FeO,Cr_2O_3) + 7Na_2O_2 \rightarrow 2Na_3FeO_3 + 4Na_2CrO_4$

Talc: $3MgSiO_3,H_2SiO_3 + 8Na_2O_2 \rightarrow 3MgO + 4Na_4SiO_4 + H_2O + 4O_2$.

Columbite is easily decomposed on heating with a mixture of sodium peroxide and sodium hydroxide (1:4).[79] Fused sodium peroxide reacts with the iron arsenides to produce arsenites and triferric tetroxide.[80] To recover metals from ores it has been suggested[48] that the finely ground material be thoroughly mixed with the peroxide and the reaction allowed to proceed at temperatures up to 500°C.; the sintered (not fused) reaction products are then leached to remove the desired components. Coke and coal are completely burnt when heated with sodium peroxide in a muffle furnace at 800°and motor fuel can also be completely oxidized.[81]

Electrolysis in an iron crucible at 450-500° (the iron crucible acting as cathode and an immersed iron rod as anode) leads to the formation of sodium ferrate and both magnetic and non-magnetic ferric oxide.[82]

On mixing the peroxide with disulphur dichloride a violent reaction ensues.[83] The following products have been detected, the relative amounts depending upon the ratio of the reactants: sodium sulphate, sodium sulphite, sodium thiosulphate, sodium sulphide, sodium chloride, sodium oxide, sulphur and sulphur dioxide.

The reaction with liquid or gaseous dinitrogen tetroxide at temperatures below 140° leads only to sodium nitrate[84] *viz.* $Na_2O_2 + 2NO_2 \rightarrow 2NaNO_3$. Nitrite is not an intermediate in this process. Above 140°, however, the reaction is more rapid and both nitrite and nitrate are produced. The effects at higher temperature are explained on the basis of the reaction between peroxide and nitric oxide *i.e.* $Na_2O_2 + 2NO \rightarrow 2NaNO_2$, the nitric oxide being formed by thermal dissociation of the nitrogen dioxide.

The effect of sodium peroxide on phosgene at $-10°$ has been investigated.[85] With excess of phosgene, sodium chloride, carbon monoxide and oxygen were obtained. A similar reaction was observed with ethyl chloroformate (ClCOOEt).

Hydrotropyl chloride (MePhCHCOCl) has been treated with sodium peroxide under a variety of conditions.[86] The products isolated, in their order of importance were phenylmethylacetic acid, $MePhCHCO_2H$; di(α,α'-phenylethyl) peroxide; MePhCHO$_2$·CHPhMe; styrene, PhCH=CH$_2$; phenylmethylcarbinol, MePhCHOH; 2,3-diphenylbutane, MePhCHCHPhMe; and acetophenone, PhAc. It has also been found that the peroxide can catalyze the isomerization of 1:8-cineole to dl-α-terpineol.[87]

Since sodium peroxide is the derivative of a weak acid (H_2O_2) it is hydrolyzed in aqueous solution. It reacts, therefore, as an alkaline solution of hydrogen peroxide and its chief uses do, in fact, depend upon this. Certain metal ions catalyze the decomposition of the aqueous solutions; these include those from iron, copper, manganese, cobalt and nickel.[88-90] The solutions as used commercially may be stabilized by a variety of substances e.g. sodium silicate, magnesium sulphate and also various substances of a protein nature.[35]

Aqueous solutions of sodium peroxide degrade starch oxidatively[91] and have been used to form peroxy-compounds, e.g. lauroyl peroxide from lauryl chloride[92] and monoperphthalic acid from phthalic anhydride.[93] In sulphuric acid, sodium peroxide reacts with phenol to produce pyrocatechol and hydroquinone, each in 25% yields.[94]

On treatment in the cold with sulphuric acid in the presence of alcohol, sodium peroxide forms the acid salt, sodium hydroperoxide (NaOOH), a rather unstable, crystalline, white solid. The hydroperoxide is capable of forming a hydroperoxidate, $2NaOOH,H_2O_2$, and its hydrated form, $2NaOOH,H_2O_2,4H_2O$.[95]

The system, Na_2O_2–NaO_2, has been examined;[4,5] this is discussed more fully later (see page 639).

Various procedures have been developed for the analysis of sodium peroxide. They include titration with potassium permanganate in the presence of boric acid as stabilizer,[96] titration with arsenious oxide,[97] gasometric determination of the nitrogen liberated from hydrazine,[98] and reaction with chlorine dioxide.[99] These methods, in general, tend to give low results owing, in part, to decomposition of the peroxide. According to Rafter[45] the best results are obtained using an oxygen evolution method carried out in acid solution in the presence of cobalt nitrate. The catalyzed decomposition to oxygen and sodium hydroxide by manganese dioxide has been employed,[59] the amount of oxygen evolved or the amount of alkali produced being estimated, as has also the catalytic decomposition to oxygen in 1 M. hydrochloric acid and 3 M. ferric chloride.[100] After a survey of the various titrimetric procedures Mattner and Mattner[101] obtained the highest and best result by the following method: to 150-200 mg. of the sample in a dry flask filled with nitrogen are added 15 ml. of 30% sodium hydroxide solution and 100 ml. of water. After the sample has dissolved 20 ml. of 20% manganous chloride solution are added and the mixture is shaken vigorously: 10 ml. of 10-20% potassium iodide solution and 25 ml. concentrated hydrochloric acid are then added, taking care to exclude air. The liberated iodine is then titrated with sodium thiosulphate. It should be pointed out that commercial samples of sodium peroxide contain sodium superoxide in amounts up to about 10% and this should be taken into account in the analyses of these samples.[54] In solution analyses involving the determination of the hydrogen peroxide produced, samples containing 10, 20 or 30% of the superoxide would appear to contain 97·2, 94·5 and 91·5% of sodium peroxide respectively. The sodium content of sodium peroxide provides a sensitive check on its composition.[54] A gasometric method for the analysis of peroxide–superoxide mixtures has been reported.[100]

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SODIUM SUPEROXIDE

For a long time it was thought that sodium could form only one higher oxide *i.e.* the peroxide. In 1947, George[1] reported that pale yellow samples of commercial sodium peroxide contain up to 10% of sodium superoxide, this conclusion being based on paramagnetic susceptibility measurements, measurements of oxygen evolution and sodium analyses. From studies of the oxygen absorption by sodium dissolved in liquid ammonia at −77°, Schechter *et al.*[2] also concluded that the superoxide can exist, and later obtained large yields by treating sodium peroxide with oxygen at high pressure.[3]

Sodium superoxide is formed by the rapid oxidation of sodium by oxygen in liquid ammonia.[2] Using a method which eliminates the side reaction of sodium with the solvent (giving amide) a mixture of superoxide and peroxide in the ratio 4:1 has been obtained.[4] By treating sodium peroxide with oxygen at 490° and at 298 atmospheres a yield as high as 92% can be obtained.[3] It has been claimed that decomposition of sodium ozonate leads to sodium superoxide.[5]

The superoxide is produced by heating metallic sodium, sodium monoxide or sodium peroxide in a closed container to at least 200°, while supplying oxygen under a pressure of at least 1500 lb./sq.in.[6] The reaction with sodium peroxide can be accelerated by the addition of a wide variety of metallic oxides; for example, at 2000 lb./sq.in. at 500°, 70% conversions were obtained in 2 hr. in the presence of cadmium oxide and titanium dioxide. The best conversions were obtained with sodium peroxide made by atomization of metallic sodium. This peroxide has a very low bulk density and a very high surface area. The sodium superoxide so prepared is stable at 65° but tends to lose its oxygen slowly at 100°. Two articles on preparative procedures for sodium superoxide have been published.[7,8]

The colour of sodium superoxide changes gradually with temperature,[3,9] from white at −100° to bright yellow at 25°. At higher temperatures the colour darkens to orange. According to Rode and Gol'der,[10] the superoxide decomposes at 120° in an atmosphere of dry oxygen and at 80–90° in dry carbon dioxide-free air.

Measurements of the gram susceptibility of mixtures of sodium superoxide and sodium peroxide and extrapolation to 100% superoxide gave a value of $\chi = 33{\cdot}0 \times 10^{-6}$ c.g.s. units.[3] This leads to an effective magnetic moment of 2·07 molar Bohr magnetons, in excellent agreement with the moments of other superoxides.

The paramagnetism of sodium superoxide is due to the presence of the radical-ion O_2^- and commercial sodium peroxide has provided a useful magnetically dilute material for studying the paramagnetic resonance absorption of this ion.[11]

Anomalous magnetic properties have been observed.[12] The magnetic susceptibilities of ~90% pure superoxide specimens were measured between 18° and −196° and a distinct maximum was found at −80°. The effective magnetic moment decreased from 2 magnetons at −80° to 0·9 magneton at −196°.

The heat capacity of sodium superoxide passes through two high peaks, at 196·5° and 223·3°K.[13] The highest heat capacities actually measured in these peak regions were 27·4 g.-cal./deg.mole at 196·23°K. and 103·50 g.-cal. /deg.mole at 223·27°K. These values are, respectively, more than 3·5 and 5 times the 'normal' values in the surrounding region. The entropy was evaluated as $S^\circ_{298\cdot16} = 27{\cdot}7 \pm 0{\cdot}3$ g.-cal./deg.mole, a value considerably larger than would have been predicted, which is partly attributable to the heat capacity maxima. The average heat capacity over the range 19°–100° is 17·13 g.-cal. /deg.mole.[14]

The heat of the solution reaction: $2NaO_2(s) + H_2O(l) \rightarrow 2NaOH(soln.) + \frac{3}{2}O_2(g)$ catalyzed by manganese dioxide has the average value, $\Delta H = -15{\cdot}9 \pm 0{\cdot}7$ kg.-cal./mole.[15] In these experiments 94% superoxide was used. From this work the heat of formation at 298·16°K. has been calculated as $-62{\cdot}1 \pm 0{\cdot}7$ kg.-cal./mole.

The crystal structure of sodium superoxide at low temperatures has been studied by powder and single crystal *X*-ray diffraction methods.[9,16,17] Three forms of the superoxide were detected. NaO_2-I is stable above −50° and has a disordered pyrite structure with $a = 5{\cdot}49$ A. at 25°. NaO_2-II exists from −50° to −77° with the pyrite structure a being 5·46 A. at −70°; the oxygen parameter is $u = 0{\cdot}43$. NaO_2-III exists below −77° with the marcasite structure, space group P_{nnm}, with $a = 4{\cdot}26$ A., $b = 5{\cdot}54$ A. and $c = 3{\cdot}44$ A. at −100°; the oxygen parameters are $x = 0{\cdot}12$ and $y = 0{\cdot}43$. The observed peaks in the heat capacity data,[13] at 196·5° and 223·3°K., correspond to the transition temperatures of these various forms of the superoxide; the transition temperatures are determined less accurately by the X-ray experiments. Zhdanov and Zvonkova[17] have also studied the crystal structures of the polymorphic forms of sodium superoxide; their unit cell dimensions for NaO_2-I and NaO_2-II are not in good agreement with the values quoted above. These authors observed that the superoxide tends to become antiferromagnetic at the transition I → II.

The differential cooling curve shows exothermic effects at −43° and −80°. The transformation at −80° takes place with the colour changing from yellow to white.[18] According to Carter and Templeton,[9] however, the colour changes on cooling do not seem to be associated with the transformations.

Thermal decomposition of the superoxide leads to a series of solid solutions.[10,19] The system, NaO_2-Na_2O_2, has been investigated[19] and samples containing about 80% NaO_2 were examined chemically, by X-ray analysis and thermographically. The thermograms disclosed a continuous endothermic effect between 120° and 250° with a gradual decomposition of the superoxide to an average component $Na_2O_{3{\cdot}60}$. Oxygen is evolved violently above 250–280° when only sodium peroxide is left behind. No sesquioxide (Na_2O_3) was detected in this system.

On exposure to atmospheric moisture sodium peroxide gives off oxygen and loses its yellow colour gradually.[3] Continued exposure to the atmosphere gives a white residue which is a mixture of sodium peroxide and sodium hydroxide, but the solid is stable indefinitely when stored in a vacuum desiccator over phosphorus pentoxide. The superoxide reacts vigorously with water according to the reaction: $2NaO_2 + 2H_2O \rightarrow O_2 + H_2O_2 + 2NaOH$, the evolution of oxygen being complete in less than three seconds.[20] Addition to a 20% acetic acid solution in chloroform also gives a quantitative release of oxygen.[3]

The reactions between the alkali superoxide and some metal salts in liquid ammonia have been studied.[21,22] Sodium superoxide is soluble in liquid ammonia to the extent of about 0·3 g./100 c.c. of solvent, but also undergoes some decomposition when stirred in this medium. The anhydrous nitrates of barium, strontium, lithium, magnesium, cadmium and zinc were allowed to react with the superoxide in the formula weight ratio necessary for complete metathesis. In all cases oxygen was evolved and the products were rich in the corresponding metal peroxide. The ammoniate of aluminium chloride and the superoxide were allowed to react in the formula weight ratio 1:3 and the following reaction scheme was suggested: $4AlCl_3,4NH_3 + 12NaO_2 \rightarrow Al_2(O_2)_3,$-$6NaO_2 + 6NaCl + 3O_2 + 4NH_3$; $Al_2(O_2)_3 6NaO_2 \rightarrow 2Na_3AlO_3 + 6O_2$. The reaction with cupric nitrate tetrammoniate in liquid ammonia gives products consisting largely of cupric oxide, hydroxide and amide.

Reduction of the superoxide by molten sodium at 500° is considerably exothermic and produces sodium monoxide.[23]

A method for the analysis of superoxide has been described.[24] The substance, on admixture with acetic acid and diethyl phthalate in a reaction cell at 0° yields oxygen only to the extent of the superoxide present; no secondary decomposition of the peroxide occurs. The reaction is: $2NaO_2 + 2CH_3COOH \rightarrow 2CH_3COONa + H_2O_2 + O_2$. This method can be used to determine superoxide in the presence of sodium peroxide.

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SODIUM OZONATE

In 1951, Nikol'skiǐ, Bagdasar'yan and Kazarnovskiǐ reported[1] that the reaction between ground anhydrous sodium hydroxide (98·2%) and ozonized oxygen (8–9%, O_3) at temperatures between –50° and –60° gave an intense yellow colour. On extraction with liquid ammonia at the same low temperature, and subsequent evaporation, a finely crystalline dark-red powder, which contained 90% NaO_3, 2–3% NaOH and 4–6% H_2O, remained.

At about the same time Whaley and Kleinberg[2] also investigated this reaction, but, finding that the products of ozonization at room temperature were not soluble in liquid ammonia or in any of the common organic solvents, they did not succeed in isolating the pure ozonate. It was observed, however, that a small amount of the yellow solid was extracted by liquid ammonia from pulverized sodium hydroxide which had been treated with ozone at –50°. Apparently traces of water are essential in order to catalyze the reaction, since it was found that ozonized oxygen did not colour anhydrous sodium hydroxide.

Nikol'skiǐ *et al.*[1] have estimated approximately that, for the rate-determining step:-

$$\mathrm{NaOH + 2O_3 \rightarrow NaO_3 + HO_2 + O_2}$$

$\Delta F^\circ_{298} = -11$ kg.-cal./mole and $\Delta H = -10$ kg.-cal./mole and that for the overall reaction:-

$$\mathrm{3NaOH + 4O_3 \rightarrow 2NaO_3 + NaOH,H_2O + 3{\cdot}5O_2}$$

$\Delta F^\circ_{298} = -92$ kg.-cal./mole and $\Delta H = -97$ kg.-cal./mole.

An effective magnetic moment of $\mu_{\mathrm{eff}} = 1{\cdot}6 \pm 0{\cdot}28$ Bohr magnetons was obtained from magnetic analysis of the products of ozonization, using the mixture law,[2] (the theoretical value for one unpaired electron being 1·73 Bohr

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magnetons).

Although sodium ozonate is decomposed by water or by acid with the evolution of oxygen, neither the solid material nor the solution after acidic decomposition gives a positive test for peroxide.[2]

There is a conflict of evidence about the stability of the ozonate. According to Nikol'skii *et al.*,[1] it decomposes at room temperatures to oxygen and sodium superoxide, $2NaO_3 \rightarrow 2NaO_2 + O_2$, the decomposition being complete in 53 hr.; during this time the colour changes from dark-red to yellow. On the other hand, Whaley and Kleinberg[2] state that the ozonate is apparently stable at room temperature, no decomposition being noted in a sample which had stood for eighteen months. Above 100° the ozonate gives off oxygen and sodium hydroxide remains: there is no indication of the formation of superoxide.

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SECTION XXIX

SODIUM HYDROXIDE

By I. DAVID

THE MANUFACTURE OF SODIUM HYDROXIDE

For many years sodium hydroxide has been one of the major products of the chemical industry. In the United States in 1944 it ranked fifth in order of tonnage produced.[1] Until the 1914-18 war nearly all the sodium hydroxide produced was made by the well-established lime-soda process. The inter-war years, however, saw the development of electrolytic methods of manufacture, and much of the increase in total output of sodium hydroxide has come from electrolytic plants. By the beginning of the 1939-45 war output was approximately the same by both methods. Since then electrolytic output has more than doubled whilst that from the lime-soda process has increased by roughly 50%.[2] This change in the industrial pattern is due largely to the demand for chlorine which has increased rapidly in the last twenty years, until in the United States its output now almost equals that of sodium hydroxide. By far the bulk of the chlorine produced is made by the electrolysis of brine in diaphragm or mercury-cathode cells where sodium hydroxide is a co-product. (Readers should consult Mellor,II,Suppl. I,pp.272-322 for details of the production of chlorine). Figures for world production of sodium hydroxide are given in Table I.[3]

TABLE I.- WORLD PRODUCTION OF SODIUM HYDROXIDE
IN 1951 × 1000 SHORT TONS

	Electrolytic production	Lime-soda Production	Total
U.S.A.	2200	605	2805
United Kingdom	400	300	700
France	115	337	452
U.S.S.R.			420
West Germany	281	110	391
Italy	54	150	204
East Germany			187
Canada	108		108
World Total			6200
U.S.A., 1946[4]	1130	743	1873

Comparison with the figure for United States production in 1946 indicates the rate of increase of sodium hydroxide production.

In addition to the more important sources of information on the chemical aspects of the sodium hydroxide industry, other papers have appeared regularly in the literature, providing information on technical processes, economic factors, and the characteristics and quality of the products.[5-18] Much technical data is to be found in the patent literature. Some reports of a general nature on the alkali industry have also been published.[19-24]

The lime-soda process

This process is based on the long-known causticization reaction:-

$$\mathrm{Ca(OH)_2 + Na_2CO_3 \rightleftharpoons CaCO_3 + 2NaOH + 1{\cdot}6\ kg.\text{-}cal.}$$

The calcium hydroxide is used as an aqueous suspension, milk of lime, and the calcium carbonate, having a lower solubility than the calcium hydroxide, is precipitated. The reaction may therefore be expressed as:-

$$\underset{\text{solid}}{\mathrm{Ca(OH)_2}} + 2\mathrm{Na^+} + \mathrm{CO_3''} \rightleftharpoons \underset{\text{solid}}{\mathrm{CaCO_3}} + 2\mathrm{Na^+} + 2\mathrm{OH'}$$

The equilibrium constant is simply expressed as $K = [\mathrm{OH'}]^2/[\mathrm{CO_3''}]$. This expression for K can be rewritten in terms of the solubility products of calcium hydroxide, S_1, and calcium carbonate, S_2: $K = S_1^{2/3}/S_2^{1/2}$. Thus, the more soluble is the alkaline earth hydroxide and the less soluble the carbonate the more effective will be the causticizing process. Moreover, since the OH term in the first equation for the equilibrium constant is squared, it can be shown that the extent of conversion of sodium carbonate to sodium hydroxide is greater in dilute than in concentrated solution. Results confirming this are to be found in Mellor,II,498 and in data compiled by Hou.[17] Recently it has been shown that with an increase in the initial concentration of the sodium carbonate solution from 10% to 23% the extent of conversion falls from 95% to 80%.[25] It has been calculated that at infinite dilution with equivalent amounts of the reactants the conversion factor is 99·6%.[26] In practice sodium carbonate solutions are used which should lead to about 94% conversion, but equilibrium is not usually reached in commercial practice and the conversion actually attained is only about 90%. The greater yields that would result from the use of more dilute solutions are offset by higher costs of processing and evaporation. It is preferable to use an excess of lime and stronger sodium carbonate solutions. A 10% excess of lime has a marked effect on the yield of sodium hydroxide.[26a]

The process is slightly complicated by the formation of the sparingly soluble double salts gaylussite, $\mathrm{Na_2CO_3,CaCO_3,5H_2O}$, and pirssonite, $\mathrm{Na_2CO_3,}$-$\mathrm{CaCO_3,2H_2O}$, both of which have been found in the precipitate and are the cause of small losses of soda.[25]

The causticization reaction is very slightly exothermic, and the equilibrium is therefore but little affected by change of temperature.[4] Some recent studies, however, appear to suggest otherwise.[26a] In practice the reaction is usually carried out at 80-90°C., the equilibrium being more rapidly established at this temperature than at ambient temperatures. The higher temperature also causes the calcium carbonate to settle more quickly and renders it easier to wash. The settling of the precipitate is also determined partly by the density of the solution.[26a] The washing of the lime-sludge is an important factor in the economic success of the process as the sodium hydroxide and unchanged sodium carbonate are tenaciously retained by the precipitate.

The lime-soda process may be carried out either batchwise or with continuous operation, and the details of the following account are taken from three main sources.[1,4,17] In batch processes soda ash is dissolved in water to give a 10-12% solution with a specific gravity of about 1·13 (17°Bé.); this is heated in cylindrical steel tanks, 10-14 ft. in diameter and 8-9 ft. deep. A number of ways of adding lime to this solution are followed in practice. It may be slaked in advance or added as lumps of quicklime. In the latter method it may be charged through a perforated steel basket which is immersed to about three-quarters of its depth in the soda solution. The lime is slaked in the basket, and the milk of lime is washed through the holes in the basket by the agitation of the soda solution. An excess of about 10% of lime is usually used. Agitation of the solution in the presence of the solid lime is maintained for about two hours after which the solid is allowed to settle, and the liquor, containing about 10% of sodium hydroxide, is removed by decantation. The lime-sludge is washed first with washings from previous batches and finally with fresh water. The wash most concentrated in alkali is used for subsequent dissolution of fresh soda or for slaking quicklime. The lime-sludge is usually dumped as waste and is seldom calcined for re-use.

A number of continuous processes are in operation, differing mainly in the treatment of the lime-sludge from the causticizer. A much stronger solution of sodium carbonate is used, containing about 18-20% of sodium carbonate, and accordingly a larger excess of lime is added than in the batch process. In some plants associated with the ammonia-soda process, sodium bicarbonate is used as a starting material. This is partly decomposed by steam in the preparation of the soda liquor, and additional lime is necessary to react with the undecomposed bicarbonate. Soda liquor and milk of lime, made up with weak washings from later stages, are fed into a series of three or more causticizers at controlled rates where they are agitated at near 100°C. so that a solution containing about 12% of sodium hydroxide results. The suspension is passed to settlers where a clear solution overflows continuously; this primary liquor is sent to the evaporators. The sludge is pumped out continuously, filtered, and the filtrate is added to the primary liquor. The filter cake is stirred in a second causticizer with a weak sodium carbonate liquor obtained as overflow from a later stage. The suspension obtained from this causticizer is passed to a settler, and the overflow, a weak caustic liquor, is used to make up the original sodium carbonate solution and the milk of lime suspension. The sludge after this second treatment is agitated with fresh water in a third stage, the liquor obtained is used in the second stage, and the solid calcined for re-use. In many plants the original lime-sludge from the first stage is subjected to a counter-current washing treatment which uses multiple tray (Dorr or Hardinge) washers or multiple tank decanters using the same general principle. A slurry of calcium carbonate is fed into the first tank of a series together with the almost clean overflow from the second tank. Solid is concentrated towards the centre of the tank whence it is pumped to the next in the series which operates in the same way. Overflow from the first tank consists of a weak caustic solution and is fed to the evaporators.

The commercial success of these processes in particular circumstances depends largely on small details of technique and minor modifications of the general process. Numerous patents covering these and articles describing them appear regularly.[27-43] More substantial changes are proposed from time to time. The causticization reaction may be done in a ball-mill, and successful conversion of concentrated solutions of sodium carbonate has been claimed.[44,45] Complete reaction in the cold in about 15 min. has been achieved by emulsifying a sodium carbonate solution with calcium oxide, but no details have appeared as to the subsequent treatment of the liquor.[46,47] The bubbling of hot air or steam through the reaction vessel has also been suggested.[48] The maintenance of a very small concentration of sodium sulphate in the reaction solution is recommended in one United States patent,[49] while in another the use of magnesium oxide, magnesium hydroxide, or a soluble magnesium salt in small amounts is described.[50] Causticization with calcined dolomite has been proposed in France.[51]

The settling of the calcium carbonate is an important factor in the lime-soda process, and it has been the subject of much study.[26a,52] A slow-settling, finely divided precipitate is obtained if the reaction temperature does not exceed 70°C.[53] The use of reaction temperatures around 80°C. or above improves the settling characteristics of the carbonate. Olsen and Direnga have made a study of the effect of temperature and of other factors such as agitation of the reaction mixture, the size of the calcium oxide particles, the amount of water used in slaking, the presence of sodium carbonate in the slaking water, and previous exposure of the calcium oxide to air.[26] The last factor leads to agglomeration of small particles of calcium oxide to larger ones followed by rapid settling of the slaked lime and calcium carbonate particles. The effect of repeated calcination of the lime has been described.[52a] The use of twice the calculated amount of water for slaking the lime caused fastest settling of the sludge, though it has also been found that the more liquid used to slake the calcium hydroxide the worse is the settling.[54] A ratio of 2 parts of calcium oxide to 1 part of water has been recommended.[26a] Again, other workers have found that a granular slaked lime, made by adding the correct amount of water at the correct temperature, or by triturating slaked lime with a strong soda solution, is the most suitable for the causticization reaction.[55-57] Calciferous shell material, suitably washed, calcined, and slaked, has also provided a suitable lime.[58] The causticizing material should contain not less than 70% of available lime and not more than 3% of magnesium oxide or the process is uneconomical.[59] The effect of the addition of various settling agents has been investigated. Electrolytes and colloidal solutions of aluminium hydroxide, ferric hydroxide, and silica slightly accelerate settling of the calcium carbonate.[57,60] The best results, however, have been reported with gelatin, starch, or raw potatoes.[26a,60,61]

The effect of sodium sulphide on the causticizing process is of some importance since it is present in various waste liquors which are treated with lime for the recovery of the sodium hydroxide. Because the sodium sulphide will itself be hydrolyzed to sodium hydroxide it is to be expected that the conversion of the carbonate to the hydroxide will be lowered, and this has been confirmed by various investigations.[26a,62-65]

Miscellaneous chemical methods for the manufacture of sodium hydroxide

In addition to the lime-soda process numerous other processes for producing sodium hydroxide have been reported or suggested from time to time. Most of these cannot compete economically with the lime-soda or the electrolytic processes except when they provide a means of using by-products or raw materials that are otherwise worthless. The possibility of causticizing sodium sulphate has received attention, and the reaction:-

$$Na_2SO_4 + Ca(CH)_2 \rightleftharpoons CaSO_4 + 2NaOH$$

has been studied at several temperatures.[66] The conversion to sodium hydroxide is 60% at ordinary temperature (20°C.) and falls with increasing temperature, being only 27% at 100°C. Very dilute solutions of sodium hydroxide are obtained. Increasing the concentration of the reactants further reduces the yield of sodium hydroxide. Partial conversion of sodium sulphate with lime has also been studied under conditions where a double salt of sodium and calcium sulphates is precipitated.[67] Again the yield of sodium hydroxide is very small, though the product, containing sodium hydroxide (*ca.* 25 g.) and sodium sulphate (*ca.* 22 g. per litre), is suitable for water softening and for decomposing straw. The addition of some fluorspar to the sodium sulphate and fusion of this mixture prior to the causticization reaction has been suggested.[68]

Barium and strontium hydroxides are possible alternatives to lime in the treatment of sodium sulphate, and 75% yields of sodium hydroxide are reported to result from boiling 30% solutions of sodium sulphate with solid barium hydroxide.[69] Strontium hydroxide may be preferable to barium hydroxide since it can be more easily regenerated by passing ammonia and carbon dioxide into the strontium sulphate suspension and calcining at 1200°C. the strontium carbonate thus obtained.[70,71] According to another method the strontium sulphate is converted into the oxide through intermediate stages of sulphide, or hydrosulphide, and carbonate.[72] In a process described for the extraction of caustic soda and alumina from salt and bauxite, one of the stages consists in causticizing sodium sulphate with barium hydroxide.[73] The following reactions indicate the process:-

$$Na_2SO_4 + Ba(OH)_2 \rightarrow 2NaOH + BaSO_4$$
$$2BaSO_4 + 2Al_2O_3 \rightarrow 2BaAl_2O_4 + 2SO_2 + 2O_2$$
$$BaAl_2O_4 + 4H_2O \rightarrow Ba(OH)_2 + 2Al(OH)_3$$
$$2NaCl + SO_2 + O_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$

The barium sulphate can be broken down if it is calcined with wood charcoal; the barium sulphide obtained is then hydrolyzed with steam at temperatures above 100°C. to form a baryta solution into which a hot solution of sodium sulphate is poured.[74] In another, similar, method of recovering the barium hydroxide, part of the barium sulphate is converted to barium thiosulphate.[74a] A barium polybasic silicate is also claimed to be effective in converting sodium sulphate into sodium hydroxide at a temperature of about 80°C. The silicate is regenerated by heating the solid reaction residue with carbon at 1400°C.[75,76]

A process which consists in heating sodium sulphate with lime and carbon in an atmosphere of nitrogen followed by treatment of the product with steam will produce sodium hydroxide with ammonium sulphate as a co-product.[77] The lime can be omitted and the sodium sulphate reduced with carbon to sodium sulphide; this is converted to sodium carbonate by being heated in carbon dioxide and then to the cyanide with nitrogen. Finally, this is hydrolyzed to sodium hydroxide at 400°C.[78,79] In another, similar, method calcium cyanamide is partially hydrolyzed to the hydroxide and the compound $Ca(HCN_2)_2$. The latter is treated with water and sodium sulphate to form calcium sulphate and $NaHCN_2$, and this can be converted into sodium carbonate by the reaction:-

$$2NaHCN_2 + 5H_2O \rightarrow Na_2CO_3 + 4NH_3 + CO_2,$$

or into sodium hydroxide by treatment with lime:-

$$2NaHCN_2 + 2Ca(OH)_2 + 4H_2O \rightarrow 2NaOH + 2CaCO_3 + 4NH_3.$$[80]

The compound $NaHCN_2$ can also be made by a fluoride method. A sodium salt is treated with hydrofluoric acid, hydrofluosilicic acid, or hydrofluoboric acid to form sodium bifluoride which when treated with calcium cyanamide yields $NaHCN_2$. This can then be hydrolyzed as before.[81]

In some methods the sodium sulphate is first reduced to the sulphide, and a solution of this is converted into sodium hydroxide by treatment with lead oxide,[82] zinc oxide,[83] copper oxide,[84] cuprammonium hydroxide,[85] ferrous oxide,[85a] or manganese dioxide.[85b] If sodium sulphide solution is made to react with sodium ferricyanide and the precipitated sulphur removed the resulting solution can be electrolyzed to regenerate the ferricyanide and to form sodium hydroxide.[86] Sodium sulphide is converted directly into sodium hydroxide in air at ordinary temperatures when it is suitably mixed with a finely divided activated charcoal. Sodium thiosulphate is formed as well, and the two are separated after extraction with water.[87] Superheated steam or a mixture of superheated steam and carbon dioxide will also convert the sulphide into the hydroxide.[88] Sodium hydrosulphide has been converted into the hydroxide by agitating a solution of it with ferric or aluminium hydroxide. The sodium hydrosulphide is obtained by mixing calcium hydrosulphide with a sodium zeolite, the calcium hydrosulphide having been made by the action of hydrogen sulphide on calcium hydroxide. The whole procedure has been conducted only on a laboratory scale.[88a]

The conversion of sodium sulphate into sodium aluminate is achieved by calcining the sulphate with alumina[89] or with a mixture of alumina and carbon.[90] The latter method has been designated the Penjakow process. The sodium aluminate is dissolved in water and the solution agitated with freshly precipitated aluminium hydroxide and then with lime to produce an alkaline liquor. Treatment of a phosphate ore containing much iron and alumina with sodium sulphate also results in formation of sodium aluminate and sodium hydroxide.[91]· A Japanese patent proposes the preliminary conversion of sodium sulphate to the sulphite by reaction with magnesium and calcium sulphites; the sodium sulphite is then causticized with lime.[92] The causticization of sodium bisulphite solutions with lime has also been considered.[93] Methods for the conversion of sodium sulphate into the carbonate are described, the carbonate being subsequently causticized with lime in the usual way.[94-96]

The merits of treating solutions of sodium oxalate with lime are not sufficient to outweigh the disadvantage that sodium oxalate is not a raw material. The preliminary preparation of the oxalate or an acid oxalate is effected by treating some other soluble sodium salt with oxalic acid,[97] a metal oxalate,[98] or a metal oxalate and a volatile alkali such as ammonia or trimethylamine.[99] Causticization of disodium hydrogen phosphate with lime has been proposed,[100] and trisodium phosphate, obtained by heating a phosphatic ore of iron and aluminium with carbon and sodium sulphate at 800°C., yields caustic soda with lime.[101] A general method of converting sodium sulphate into a more easily causticized salt such as the phosphate, oxalate, sulphite or fluoride consists in causing sodium sulphate to react with calcium phosphate, or one of the other calcium salts, in the presence of an excess of sulphuric acid or orthophosphoric acid.[102]

The causticization of sodium fluoride is a possible means of making sodium hydroxide, and several patents and articles have been devoted to ways of obtaining the fluoride, chiefly from sodium chloride. Some of these methods involve the formation of sodium fluosilicate as an intermediate by reactions such as:-

$$CaF_2 + SiF_4 + 2NaCl \rightarrow Na_2SiF_6 + CaCl_2.$$

An acid is usually present.[103-110] Alternatively, sodium chloride can be treated with zinc fluosilicate.[111,112] The sodium fluosilicate is then thermally decomposed to sodium fluoride and silicon tetrafluoride, or it may be treated with ammonia to produce sodium fluoride, ammonium fluoride and silica, and the mixed fluorides are then causticized.[113] Sodium fluoride can also be obtained by the reactions between sodium chloride and ammonium fluoride,[109,110,114-116] sodium chloride and potassium fluoride,[117] sodium chloride and hydrogen fluoride,[118,119] and, presumably, between clay, sodium chloride, and hydrogen fluoride.[120] The sodium fluoride thus produced is causticized with calcium hydroxide at about 80°C.,[121-123] though other causticizing agents such as barium hydroxide can be used.[118,124]

A method proposed originally in 1882 by C. Löwig and referred to in Mellor,II,497 uses ferric oxide as the causticizing agent with sodium carbonate. It has not competed successfully with the lime-soda method, but there has been some revival of interest in the process over the last thirty years, and a number of patents and articles dealing with it have appeared.[125-130] The process consists in heating sodium carbonate with ferric oxide until all the carbon dioxide has been driven off and a residue of sodium ferrite remains. When this is treated with hot water, hydrolysis occurs whereby a solution of sodium hydroxide is produced and ferric oxide is precipitated and can be used again. Caustic soda solution and water are used in turn for the decomposition of the ferrite in such a way as to render the sodium hydroxide free from sodium carbonate and sodium sulphate which are precipitated.[131] A detailed study of the process has been made by Matsui and others. If 1·8 parts of ferric oxide are used with one part of sodium carbonate the ferrite is formed rapidly at about 700°C. and is hydrolyzed completely at 70°C.[132] The dissociation pressure of sodium carbonate in the presence of ferric oxide is calculated to be 1 atm. at 849·1°C., and the heat of reaction at 25°C. $(-\Delta H_{298\cdot 1})$ is 34,479 g.-cal.[133,134] The formation of the ferrite has also been studied by Sokolov who concludes that various ferrites may be formed according to the ratio Na:Fe in the reaction mixture, but that the ferrite most likely to be formed is $NaFeO_2$.[135] The optimum temperature for ferrite formation has been found in practice to be 850°C. The higher rate of formation theoretically expected at higher temperatures is not realized in practice owing to a decrease in the porosity of the ferric oxide. It seems that the formation of the ferrite and its subsequent hydrolysis take place on the surface of the ferric oxide, and it is possible to carry the process through several cycles without destroying the supporting skeleton of ferric oxide.[136] A study of several factors in the formation of sodium ferrite indicates that the surface area of the reactants is the most important.[137] Iron ores containing sufficient ferric oxide are suitable for formation of the ferrite.[138] The use of titanomagnetites has been examined: higher reaction temperatures are necessary and lower yields are obtained, but the non-ferrous metals are set free from the ore.[139] In an interesting variant of the Löwig process stannic oxide is heated with sodium carbonate at 1100°C., and the sodium stannate thus formed is dissolved in water in an autoclave and there hydrolyzed between 180° and 374°C., sufficient pressure being maintained to ensure that a liquid phase persists. Yields of 80% are reported.[140] Sodium chromite is presumably produced when sodium carbonate is heated with chromic oxide in a non-oxidizing atmosphere, and this can also be hydrolyzed to sodium hydroxide.[141] Sodium aluminate is produced from nephelite concentrates which have been roasted with limestone and leached with hot sodium carbonate solution. It is converted into sodium carbonate for causticization by the usual methods.[142,143] Sodium aluminate can also be obtained from clay and sodium chloride.[144] Sodium bicarbonate may be used with advantage instead of sodium carbonate in the normal ferric oxide methods.[144a]

The causticization of sodium nitrate by means of ferric oxide, referred to in Mellor,II,497, has received little further attention.[145-147] The corresponding reaction with sodium sulphate is not likely to be commercially feasible in view of the high temperatures, around 1450°C., that are necessary.[148]

If sodium cyanide is hydrolyzed with steam at 400°-500°C. sodium hydroxide, sodium carbonate and ammonia are formed. This reaction has been the subject of a number of patents on the manufacture of sodium hydroxide.[149-159] If the cyanide mass is spread out in thin layers to facilitate the action of the steam and the carbon dioxide formed is removed rapidly the amount of sodium carbonate formed is reduced.[160-162] The sodium cyanide can be made by heating sodium carbonate or bicarbonate from the ammonia-soda process with carbon and nitrogen at a high temperature. Sodium sulphate also gives the cyanide when heated with carbon and nitrogen,[163] or with carbon, nitrogen and lime.[164]

Molten sodium chloride can be hydrolyzed with superheated steam in the presence of a catalyst; platinized asbestos[165] and pumice stone have been recommended.[166] Sodium nitrate can be hydrolyzed catalytically in a similar way.[167] Sodium chloride can be converted into the hydroxide by reaction with barium hydroxide in aqueous solution in conditions in which a basic barium chloride is precipitated. The reaction can also be effected in aqueous alcoholic or in aqueous ammoniacal media.[168-171] The conversion of sodium carbonate into the hydroxide with steam at a high temperature and pressure remains a possible method.[172] The use of strontium or barium hydroxides as causticizing agents has been considered but does not seem to have been developed.[173] Sodium arsenate formed in the treatment of a cobalt ore has been converted into sodium hydroxide by hot milk of lime.[174] The production of sodium hydroxide by the action of steam on sodium is described in an American patent. Molten sodium is fed continuously on to a pool of molten anhydrous sodium hydroxide through which an excess of steam is passed upwards. The hydrogen produced is carried away with the surplus steam, and sodium hydroxide is withdrawn from the pool continuously.[174a] If sludges resulting from the electrolytic production of sodium are heated with silica, vapours of sodium monoxide are formed and can be passed into water to produce solutions of sodium hydroxide.[174b]

It has been suggested that caustic soda solutions suitable for treating vegetable materials could be obtained in the cold by repeatedly passing a solution of calcium hydroxide over a sodium zeolite.[175] More recently the possibility of producing sodium hydroxide by ion-exchange methods has been considered. When the exchange resin Dow HCR, saturated with sodium ions, is brought into contact with a solution of strontium hydroxide the resulting solution may contain as much as 35% of sodium hydroxide. The strontium still in the solution can be precipitated as a basic chloride and reconverted to strontium hydroxide. It seems that other bases cannot be used in place of strontium hydroxide; barium hydroxide is molecularly adsorbed on the resin and forms a precipitate of $Ba(OH)_2,NaOH$, removing sodium hydroxide from the solution. The resin can be recharged by treatment with sodium chloride. Other resins have been found to be unsuitable.[176] A Japanese patent proposes the extraction of sodium from sea-water with an ion-exchange resin. Sodium ions absorbed on the resin are removed with sulphuric acid, and the sodium sulphate solution obtained is electrolyzed to produce sodium hydroxide.[177] An anion-exchange method that has been devised utilizes sodium chloride and lime as the raw materials. Sodium chloride, in a solution containing not less than 10%, is made to exchange with a hydroxyl-exchange resin of the Amberlite type, and sodium hydroxide solutions containing as much as 20% of sodium hydroxide can be produced. The resin is regenerated with a solution of calcium hydroxide.[177a-c]

Electrolytic methods of manufacturing sodium hydroxide

The production of sodium hydroxide by electrolytic methods (see also Mellor,II,Suppl. I,pp.273–312) involves the electrolysis of brine with the resulting formation of chlorine at the anode and hydrogen and an alkali hydroxide solution at the cathode:-

$$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2 + H_2.$$

Most of the developments of the process have been concerned with the separation of the cathode products from the rest of the cell. This has been achieved in two ways. In one the cathode is surrounded by a porous diaphragm of some suitable material which permits the passage of ions but prevents the diffusion of alkaline liquor formed around the cathode back into the main body of the cell. A 10–12% solution of sodium hydroxide is drawn off. In the other method the cathode consists of a moving stream of mercury at which sodium ions are discharged to form a sodium amalgam. This is led to another chamber where it is decomposed by water with the formation of hydrogen and an approximately 50% solution of sodium hydroxide. American practice has so far favoured the diaphragm cell, though recently there has been a growing interest in the development of mercury cells.[178] German industry, on the other hand, has favoured the mercury cell. Developments in sodium hydroxide production in Germany during the second World War are dealt with in the various Allied Technical Reports.[179] The cost of production appears to be approximately the same by both processes, but the mercury cell produces sodium hydroxide of higher purity.[178] The sodium hydroxide liquor obtained from mercury cells is much more concentrated than that from diaphragm cells and requires less evaporation.

The raw material for diaphragm cell operation may be the solid salt or natural brine transported as liquid by pipeline from the well-head to the plant. The latter source is frequently employed in the United States. For the mercury cell process it is more desirable to use the solid salt,[179] and this may account in part for the development of this process rather than the diaphragm cell process in Europe where deposits of rock salt are more easily available. Filtered sea-water has recently been used for diaphragm cell feed in Japan.[180,181] The cell feed is usually a saturated salt solution, but the possible advantages of using solutions which are, presumably, supersaturated has been considered.[182] Purification of the brine is an important preliminary in both processes. Complete removal of calcium and magnesium is essential in order to prevent blockage of the diaphragms by precipitated calcium and magnesium hydroxides. Calcium can be eliminated by addition of a soluble sulphate.[183] Removal of heavy metals is necessary for the same reason and in order to avoid contamination of the final product. Their presence in feed to mercury cells can be particularly harmful since they may plate out on the mercury and lead to difficulties through 'thick mercury' and 'mercury butter' formation. A detailed study of the effects of various metals on the efficiency of the mercury cell process has shown that magnesium, calcium, barium, iron, nickel, copper, zinc, lead and arsenic in very small concentrations in the brine feed have no effect. Vanadium, molybdenum, chromium and titanium, however, caused a fall of 4-5% in the current efficiency.[183a] Sulphate can be tolerated up to a concentration of about 10 g. per litre, though it is usually removed by adding calcium or barium chloride or barium carbonate.[184] A method of separating sodium sulphate from solid salt consists in centrifuging the impure salt and simultaneously washing with brine containing sodium hydroxide as a surface active agent. The sodium sulphate is then removed from the brine by cooling the solution.[184a] Chlorine in the brine tends to interfere with the precipitation of heavy metals, and it is necessary to dechlorinate brine after its passage through the cell and before it is resaturated and recycled. In general, purification is more important and more extensive in mercury cell practice.[184b]

The voltage of an electrolytic cell depends on the decomposition voltage of the salt, the length of the electrolytic path, the overvoltage at each electrode, and the current density in the cell. With a diaphragm cell the resistance of the diaphragm is an additional factor. The hydrogen overvoltage at a steel or iron cathode is 0·08 V. The very high hydrogen overvoltage at a mercury cathode has made possible the development of the mercury cell process, since for this reason sodium is discharged preferentially at the cathode and sodium amalgam is only slowly decomposed by water. Chlorine overvoltage varies also with the anode material, being low with carbon electrodes and high with platinum or magnetite, these three materials being those chiefly used in practice. Cell voltages work out in practice at 3·3-3·5 V. for diaphragm cells and 4·3 V. for mercury cells.[2] The efficiency of the cell may be impaired in a number of ways. One of these, the occurrence of secondary reactions in the solution at the electrodes, has been studied in diaphragm cells by Murray and Kircher.[185] Electrolyte reaching the cathode contains dissolved chlorine, and this reacts with the sodium hydroxide in the following way:-

$$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$$

$$\begin{aligned} Cl_2 + H_2O &\rightarrow HCl + HClO \\ 3Cl_2 + 6NaOH &\rightarrow NaClO_3 + 5NaCl + 3H_2O \\ NaClO + 2HClO &\rightarrow NaClO_3 + 2HCl \end{aligned}$$

More important are reactions at the anode caused by migration of hydroxyl ions through the diaphragm:-

$$\begin{aligned} 4OH' - 4e &\rightarrow O_2 + H_2O \\ 4OH' - 4e + C &\rightarrow CO_2 + 2H_2O \\ 6ClO' + 3H_2O - 6e &\rightarrow 2ClO_3' + 4Cl' + 6H^+ + 1\tfrac{1}{2}O_2. \end{aligned}$$

In mercury cathode cells electrolytic reduction of chlorine and hypochlorous acid can lead to current losses of 25%. Higher current densities reduce this loss, but it is not affected by the width of the anode-cathode gap or by the pH of the feed brine. The effect of small additions of chromate ion has also been studied.[185a] Increased current efficiency can also be achieved by exposing the mercury cathode to ultrasonic waves of 8000 kilocycles.[185b] Extensive accounts of both processes are to be found in Mellor,II,Supplement I in the section on the manufacture of chlorine and in other major works of reference all of which include large bibliographies.[1,4] It is interesting to note that in the early years of the development of electrolytic methods few cells of either type were commercially successful.[186] That they have become so is due partly to development in design and partly to the great and increasing demand for chlorine.

Diaphragm cell methods

From analyses of feed and product liquors it has been shown that a volume decrease takes place during the electrolysis and for complete conversion would be as high as 20·4%. It is accounted for by consumption of water in the reaction and by the greater volume contraction on solution of sodium hydroxide as compared with sodium chloride. High current yields are possible if proper control of the concentration of both feed and product liquors is maintained, though yield is unaffected by factors such as current density and the shape of the cathode.[187]

A large number of diaphragm cells has been developed.[1] They are of three main types: (*a*) those containing vertical unsubmerged diaphragms, (*b*) those containing vertical submerged diaphragms and (*c*) those containing horizontal unsubmerged diaphragms. In general, the vertical diaphragm cells consist of an outer steel tank, cylindrical or rectangular, which supports a cathode of a perforated iron plate or woven iron screen a short distance inside. Advantages for the cylindrical type were claimed as far back as 1919.[188] Both tank and screen are cathodic and are usually lined with a layer of asbestos. Graphite anodes face the diaphragm at a minimum distance. An inert insulating cover carrying the brine inlet and chlorine outlet closes the cell. Brine is maintained in the anode compartment at a level above the upper edge of the cathode. It percolates through the diaphragm into the cathode compartment where a lower level of dilute sodium hydroxide solution is maintained in the submerged type of cell and where it drips off the bottom in the unsubmerged type of cell. In either case the hydrogen formed at the cathode is led off from a connexion near the top of the outer tank. Cells with horizontal diaphragms usually consist of a rectangular steel or concrete tank supporting a horizontal diaphragm and a woven iron cathode. Cells with horizontal diaphragms yield a stronger caustic liquor than do the vertical diaphragm cells.[4] The diaphragm again consists of asbestos fibre, sometimes mixed with barium sulphate. These various diaphragms gradually become clogged with solid impurities in the brine and have to be renewed periodically.

Anodes are usually of artificial graphite. The graphite is slowly used up, owing, it is believed, to hydroxyl ion discharge and consequent oxidation. Impregnation of the anode with linseed oil was once practised;[188] at present, in the United States at least, anode manufacturers impregnate the graphite according to proprietary processes. The electrolysis is usually carried out at 80–90°C.

Of the diaphragm cells now used in the United States by far the most important is the Hooker S cell, which has been developed from the Marsh cell and represents a considerable advance on earlier types.[189,190] For details of the Hooker S cell the reader should consult Mellor,II,Supplement I,276, other works of reference,[1,4] and the accounts of the inventors.[185,191,192] The outstanding feature of the cell is the design of the cathode which consists of an outer and an inner wall between which the hydrogen and the caustic liquor are collected. From opposite sides of the inner wall, which is perforated, narrow fingers of nearly the same depth as the anodes project into the body of the cell. These fingers are themselves perforated and are arranged to fit between the anode plates, and they form the active cathode surfaces. The perforated surfaces are covered with an even layer of asbestos fibre. This cathode is easy to clean when it becomes blocked in use. An important feature of the performance of the cell is the high concentration of caustic liquor obtained and the low concentration of chlorate. Typical operating figures are given in Table II.[4]

TABLE II.· OPERATIONAL DATA FOR THE HOOKER S CELL

Current per cell	6000–7000 amp.
Voltage per cell	3·35 V.
Current efficiency	96%
Voltage efficiency	69%
Energy efficiency	65%
Temperature of feed brine	90°C.
NaOH in cell liquor (product)	135 g. per litre
$NaClO_3$ in cell liquor	0·07 g. per litre
Active cathode surface	130 sq. ft.
Active anode surface	110 sq. ft.
Life of diaphragm	200 days
Life of anodes	450 days
Output of NaOH per cell per day	450–530 lb.
Output of Cl per cell per day	400–470 lb.

Larger cells carrying about 30,000 amperes are in operation. (See Mellor,II, Supplement I,276,277). The current efficiency of a diaphragm-cell can be calculated from the output of chlorine, and methods of determining the latter have been reported.[192a,b]

Second in importance in American industry appears to be the Vorce cell.[1,193,194] This is a cylindrical cell with a vertical unsubmerged cathode bearing a diaphragm of asbestos 0·06 in. thick. The cell is operated at 1000–1500 amp. When the diaphragm is new the cathode effluent contains about 85 g. of sodium hydroxide per litre, but with ageing of the diaphragm the concentration rises gradually to about 105 g. and even 120 g. per litre. The Siemens-Billiter cell has been used extensively in Germany.[4,195] This has a horizontal cathode, and the diaphragm consists of a fibrous material, asbestos, and a powder, barium sulphate, which are spread uniformly on a sheet of asbestos cloth resting on the diaphragm support. Variation in the alkalinity of the cathode liquor is achieved by altering the level of brine in the cell. The concentration of the cathode liquor is in the range 12-16%. The cell operates at 4-5 V. and 6000 amp.[195a] A cell capable of producing alkali containing 25% of sodium hydroxide was described by de Nora in 1924, but it has not been put into widespread use.[196] It has a vertical cathode, and the cathode spaces are empty of liquid. The operation of Nelson cells in a Canadian plant has been described.[197] This cell, which has had widespread use in the United States in the past, has a vertical U-shaped cathode carrying a diaphragm of asbestos paper. Descriptions of the many diaphragm cells developed over the past 30-40 years are given in the main works of reference on applied chemistry and in a number of patents and articles.[1,4,198-215]

Attempts to improve the characteristics of the diaphragm are made from time to time since the main loss in current efficiency is due to diffusion of hydroxyl ions from the catholyte through the diaphragm into the anode compartment. It will be realized from the foregoing description of some cells that asbestos paper or fibre is in most common use either alone or mixed with a powdered material such as barium sulphate. Loose granular material spread evenly over thin asbestos cloth has been proposed, and it is possible to use sodium chloride itself for this purpose.[216] Cotton cloth, paper and other organic substances not readily decomposed by alkali;[217] quartz, corundum, cellulose[218] and polyvinyl chloride[219] have all been suggested as diaphragm materials. Recently it has been found that an ion-exchange resin (such as melamine resin) used as a diaphragm will prevent the movement of hydroxyl ions produced at the cathode towards the anode.[220] Sodium hydroxide free from sodium chloride is said to be made by using a diaphragm having layers of copper ferrocyanide, copper silicate and calcium silicate formed successively on a support of unglazed porcelain.[221] The use of a diaphragm is abandoned entirely in a proposed Japanese process in which electrolysis of brine is carried out in the presence of bentonite which absorbs the chlorine at the anode.[222]

Mercury-cathode cells

Descriptions of the various mercury-cathode cells in past and present use are to be found in reference works on applied chemistry and in several patents and articles.[1,4,215,223-233] The extensive war-time developments in Germany have been collected in the Allied Technical Reports.[179] The Mathieson cells developed in recent years in the United States are particularly important.[234] Their operation is described in the section on the manufacture of chlorine in Mellor,II,Supplement I,293. The Kellner-Solvay cell and variants of it have found widest application in Europe. In this cell the mercury flows continuously along the cell floor.[4] Vertical cells have been developed, especially in Germany, with the object of saving floor space.[178,234a] Forms of the de Nora mercury cell which are capable of carrying currents of 48,000 amp. have been described.[234b, c] In general a modern mercury-cathode cell consists of a trough, 25-50 ft. long and 20-40 in. wide, constructed of steel which forms the cathode connexion. A thin stream of mercury which forms the active cathode surface flows along the bottom of the tank which is sloped for the purpose. In the Castner-Mathieson cell, developed from the original Castner cell, the mercury flows back and forth under a sealing wall as the cell is slowly rocked through a small angle. Graphite anodes hang horizontally just above and parallel to the mercury surface and are grooved or perforated to allow the chlorine to escape. Platinum and magnetite anodes, recommended in the past, are no longer used. Saturated brine is fed into the tank to form a deep layer above the mercury, and the flow is adjusted so that it overflows with a sodium chloride content of about 20–26%. It is usually freed from chlorine, resaturated with dry sodium chloride and returned to the cell. Owing to its high overvoltage on mercury there is no discharge of hydrogen at the cathode; instead a weak sodium amalgam is formed. The amalgam usually contains about 0·2% of sodium, that formed in a Castner-Mathieson cell containing rather less.

The amalgam is led to a secondary cell or 'denuder' where it forms the anode, and the cell itself, constructed of some material with a low hydrogen overvoltage, forms the cathode. Iron or steel is suitable for this purpose.[235] Such material tends to become amalgamated, and to prevent this the cell is separated from the amalgam by carbon or graphite, which may be of elaborate construction to provide a large active cathode surface.[236,237] The electrolyte is a sodium hydroxide solution. The denuder may consist of one compartment only or of a series of compartments through which the amalgam and the electrolyte pass in opposite directions.[238-241] The sodium hydroxide liquor leaving the denuders usually contains about 50% of sodium hydroxide, but this can be varied by altering the temperature in the cell.[238] Liquors containing 74% of sodium hydroxide can be obtained with 3-stage cells operating on the counter-current method.[241a] Greater purity of the liquor is claimed if the amalgam is given a preliminary wash with water before being fed to the denuders.[242] The use of catalysts and contact agents to aid the decomposition of the amalgam has been studied. Transition metals and their alloys appear to be the most effective.[243-247] Some of these will promote the decomposition of the amalgam with ethyl alcohol.[244] The period of deamalgamation is shortened if the amalgam is exposed to ultrasonic waves of 500 kilocycles.[247a] The temperature of the electrolyte in the denuder varies according to the details of the operation and depends also on whether a catalyst is employed. A considerable variation is thus possible in practice, and temperatures between 30° and 120°C. are quoted. Some figures for the operation of mercury-cathode cells are given in Table III.[1]

TABLE III. - OPERATION OF MERCURY-CATHODE CELLS

Cell voltage	3·8–4·9 v.
Current per cell	1500–40,000 amp.
Anode current density	30–350 amp. per sq. ft..
Current efficiency	91–96%
Energy efficiency	48–60%
Output of sodium hydroxide	0·6–0·7 lb. per kw.-hr.
Output of chlorine	0·53–0·62 lb. per kw.-hr.
Concentration of sodium hydroxide liquor	30–70%

Mercury cathode cells in which the cathode is stationary have recently been described. Separation of the anode and cathode regions of the cell becomes necessary as in conventional diaphragm cells.[247b, c]

Miscellaneous electrolytic methods

The use of electrolytes other than sodium chloride has received consideration from time to time. The most important alternative to sodium chloride is sodium sulphate. This is a by-product of the viscose rayon industry which is the biggest consumer of sodium hydroxide. When an aqueous solution of sodium sulphate is electrolyzed, sodium hydroxide and hydrogen are formed at the cathode and sulphuric acid (or sodium bisulphate) and oxygen at the anode. The sodium sulphate from viscose waste liquors is isolated by evaporation and crystallization of the liquors and is then made up to a solution containing 30–40% of Na_2SO_4.[248,249] This solution is electrolyzed in diaphragm or mercury cells since the same problem of separating anode and cathode products exists as in the electrolysis of sodium chloride. Sulphuric acid formed in the anode compartment can be absorbed on a suitable resin and in this way effectively separated from the cathode product.[249a] The elaborate design of the latest diaphragm cells used for sodium chloride electrolysis has not been developed for sodium sulphate, and cells of simpler construction have been studied and used. Diaphragms may be of microporous ebonite, asbestos or microporous rubber, and they may be vertical or horizontal.[249-251] Cathodes are of iron, platinum or copper, and anodes are of platinum, lead or carbon, though the best results have been achieved with anodes of lead–silver alloys.[248,249,252] The solubility of sodium sulphate in water decreases sharply with increasing alkalinity, and consequently difficulties due to clogging of the diaphragm with solid sodium sulphate have been experienced. The use of the mercury-cathode cell is therefore favoured, though this also requires a diaphragm round the anode.[251,253] Electrolysis at a temperature of 40°C. in a mercury-cathode cell with an anode of a lead-antimony alloy yields sodium hydroxide solution of very high quality.[254] High efficiency for the process is claimed if a layer, 1·5–2 cm. thick, of solid sodium sulphate decahydrate is maintained over the mercury cathode.[255,256] A cell with a cathode of a copper amalgam and an anode of a bismuth amalgam has been described. The sodium is discharged at the cathode as an amalgam, and the sulphate forms insoluble bismuth sulphate at the anode.[256a] Costs in these sodium sulphate processes are somewhat higher than in the electrolysis of sodium chloride, and there is the added disadvantage that relatively cheap co-products, sulphuric acid and oxygen, are obtained.[257-260]

The electrolysis of molten sodium sulphate has been studied.[261] Ferric oxide coated on to metal cathodes yielded sodium ferrite in the electrolysis, and this was subsequently hydrolyzed to give a solution of sodium hydroxide. If a lead cathode was used a lead–sodium alloy was formed. Electrolysis of sodium sulphide solutions in mercury-cathode cells of the Castner-Kellner type yields sodium hydroxide free from carbonate.[262] Electrolysis of sodium nitrate and nitrite solutions yields ammonia and sodium hydroxide.[263] Sodium carbonate, in spite of its availability, has only recently been considered for electrolytic production of sodium hydroxide. Electrolysis of a sodium carbonate solution of appropriate strength in a diaphragm cell at 60–80°C. produces a sodium bicarbonate solution at the anode and a sodium hydroxide solution containing about 25% of sodium hydroxide at the cathode. The anode liquor is drawn off, cooled to precipitate sodium bicarbonate, made up to strength, and returned to the cell.[264] Sodium carbonate solutions can also be electrolyzed in mercury-cathode cells.[264a] A major objection to the use of sodium carbonate as an electrolyte is its relatively low solubility. Attempts to overcome this have been made by electrolyzing solutions of sodium carbonate containing sodium sulphate, chlorate or nitrate. Cathode liquor containing as much as 45% of sodium hydroxide can then be obtained.[265] Sodium acetate solutions can be electrolyzed in cells of the mercury-cathode type with magnetic ferric oxide as the anode.[265a, b] A process for electrolyzing sodium chromate solutions employs a simple diaphragm cell, and sodium hydroxide is formed at the cathode and chromic acid at the anode. Conditions are so arranged that both these solutions have a lower density than the sodium chromate solution and thus float separately on the latter in the cathode and anode compartments. Mixing of the cathode and anode products is thereby avoided.[266-268]

Evaporation of sodium hydroxide solutions

Since the initial product from the lime-soda process and from diaphragm cells is an aqueous solution containing about 10-12% of sodium hydroxide, it is evident that further evaporation to more concentrated solutions or to solid sodium hydroxide is a matter of considerable importance in the industry. The liquor from mercury-cathode cells is a 50% sodium hydroxide solution and, in the United States especially, it is customary to use this without further treatment. It is suitable for direct use in the viscose rayon industry, which is the largest consumer of sodium hydroxide, and it may be piped short distances or transported by tank-car or barge.[269] Owing to the readiness with which a 50% solution of sodium hydroxide solidifies at low temperatures these cars must be thermally insulated.

Evaporation of liquors from diaphragm cells and from the lime-soda process and of all liquors to concentrations greater than 50% was formerly done in open pots heated directly. Modern plants use steam-heated, multiple-effect evaporators designed to give maximum efficiency and to overcome the corrosion problems inherent in treating concentrated sodium hydroxide solutions.[1,4,270-279] Evaporation is also achieved effectively if the solution is passed as a thin film over a surface heated by radiation[280] or over the surface of a hot liquid mass such as molten lead.[281] The evaporators are sometimes operated at a low pressure, and solid anhydrous sodium hydroxide may then result without the necessity for the final 'caustic finishing'.[282-285] By heating 70% liquor at 380°C. under a pressure of 20 in. of mercury a sodium hydroxide containing about 1% of water can be obtained.[285a] The low pressure may be varied continuously during the evaporation so that the boiling point of the melt approaches but does not fall below the temperature of the commencement of crystallization.[286,287] In one process a liquor of 'technical concentration' is first boiled under a pressure of 70 mm. Hg until it reaches a concentration of about 80%, then under a pressure of 520-600 mm. Hg until it reaches a concentration of about 91%, and finally at 70 mm. Hg again until all the water in the melt is removed.[288] Steam-drying has been successfully carried out by cascading the sodium hydroxide solution over trays against a counter-current of steam at temperatures between 260° and 425°C.[289] The large amount of heat available in concentrated solutions of sodium hydroxide can be utilized for the partial removal of water from dilute solutions by passing the former into the latter after it has been raised to a sufficiently high temperature in the concentration.[290,291] Molten anhydrous sodium hydroxide can also be used to heat sodium hydroxide solutions which in this way can be concentrated to 90% sodium hydroxide.[291a] The heat generated in the decomposition of sodium amalgam in the denuders in a mercury cell plant is sufficient to evaporate a sodium hydroxide solution to a concentration of over 80%.[278] Dehydration can also be effected by direct exposure to burning hydrogen[292] or by treatment with sodium oxide.[293] It has been shown in the account of the lime-soda process (see page 643) that the conversion of sodium carbonate is lower in concentrated than in dilute solutions. However, a more concentrated sodium hydroxide liquor results if the reaction is accomplished in concentrated solutions. Moreover, if an oxide is used as the causticizing agent instead of a hydroxide, further concentration results through the consumption of water in the reaction. The possibility of using strontium oxide as the causticizing agent in the presence of insufficient water to convert all of it to the hydroxide during the reaction has been considered.[294]

The final evaporation to produce anhydrous sodium hydroxide - known as 'caustic finishing' - is still carried out extensively in the industry in large, open, hemi-spherical, cast-iron pots heated directly.[1,4,295] There are two processes, the 'single-pot' and the 'back-pot' process. In single-pot operation the entire finishing is completed in one pot, the final dehydration temperature being about 500°C. The back-pot system involves two pots, one to receive the feed liquor, where most of the evaporation is done, and a second for the last stages of the evaporation at the higher temperatures. A system employing three pots has been described.[296] Rotary tubes of silver have been used for the final dehydration and fusion, and a purer product is probably obtained.[297]

In addition to the older, well-established methods of evaporation and dehydration other, rather more elaborate, methods have been studied. Anhydrous sodium hydroxide can be obtained from 40% solutions by passing the latter slowly down vertical silver tubes which are maintained at about 500°C. at the top and 300°C. at the bottom.[297a, b] The use of a vapour stable at high temperatures, such as diphenyl vapour, as the heating medium has been found effective in concentrating sodium hydroxide solutions to more than 98%.[298] The most promising advance on current practice seems to be in the development of methods of azeotropic distillation. This is in effect a reversal of the method of steam-distillation familiar in organic chemistry. In laboratory experiments, using kerosene boiling in the range 180-272°C. as the diluent, it has been found that with 2 parts of kerosene to 1 part of sodium hydroxide solution dehydration can be effected at about 220°C. instead of the 500°C. required with open pots.[299] Sodium hydroxide is left as a solid suspension in kerosene; it can be filtered and washed with solvent naphtha until it retains about 0·1% of kerosene. Calculations of the heating costs indicate a reduction to about one-third the usual costs. In addition the sodium hydroxide is formed as a fine free-flowing powder, a highly desirable product, and corrosion of equipment is avoided because of a protective film of kerosene. Developments and modifications of the first experiments have been reported.[301,302] Polychlorinated, polybrominated and nitro-aromatic hydrocarbons, and organometallic compounds such as dipropyl mercury are also suitable for these azeotropic distillations.[303] Still further improvement results if a mixture of one of these high boiling liquids with a low boiling hydrocarbon is used. Heating of sodium hydroxide solutions in the presence of an inert gas so that the partial pressure of water vapour is reduced and the evaporation effected at a lower temperature, has also been considered.[302,304] Liquor from diaphragm cells can be concentrated to about 50% sodium hydroxide by electrolysis under the right conditions. Difficulties are encountered, however, through the decomposition of the sodium chloride also present in the liquor.[305] Very dilute sodium hydroxide solutions such as weak wash liquors can be concentrated slightly by absorbing the sodium on a resorcinol resin and eluting with less water. The process is suitable for recovery of wash liquors in the manufacturing processes.[306]

The transportation of sodium hydroxide solutions has already been mentioned. Solid, anhydrous sodium hydroxide is usually transported in cylindrical metal drums into which the molten, anhydrous material is poured. Arrangements may be made for splitting the drum-load into smaller cakes.[307] If a small quantity of paraffin or a heavy motor oil is put into the drum before the molten sodium hydroxide is poured in a fibrous, crystalline structure develops on solidification. The product is then easily crushed and broken.[308] For use in smaller quantities, sodium hydroxide is made available in stick or flake form. To obtain the latter, molten anhydrous sodium hydroxide is solidified on a cooled revolving drum and removed therefrom by a mechanical scraper.[309] Granulated sodium hydroxide can be made by pouring the molten material through a sufficient height in an inert atmosphere.[310-312] Powdering of sodium hydroxide is difficult owing to its hygroscopic nature. It can be powdered under an oil which is subsequently removed by heating.[313]

Purification of sodium hydroxide

The main impurities in commercial sodium hydroxide are sodium carbonate, sodium chloride, sodium sulphate and sodium silicate. Sodium hydroxide made in diaphragm electrolytic cells also contains a small percentage of sodium chlorate, and this is particularly objectionable in the rayon industry, the chief user of sodium hydroxide. Analytical figures obtained with materials manufactured in the United States are given in Table IV.

TABLE IV.- ANALYSIS OF U.S. COMMERCIAL CAUSTIC SODAS[1]

Per-cent. of consti-tuent	Lime-soda plants 50% liquor			'Un-treated' dia-phragm cell 50% liquor	Mercury cell 50% liquor	Anhy-drous	Usual 'rayon quality' specifi-cation
	1920	1930	1940				
NaOH	47·0	49·0	50·0	50·0	50·0	98·5	50·0
Na_2CO_3	0·12	0·12	0·10	0·65	0·1	0·60	0·20
Al_2O_3	}0·022	}0·02	0·003	0·001	0·0006	0·0005	0·003
Fe_2O_3			0·0008	0·010	0·0003	0·0015	0·0005
NaCl	0·28	0·25	0·14	1·0	0·1	0·30	0·15
Na_2SO_4	0·12	0·10	0·04	0·2	0·01	0·25	0·07
SiC_2	0·20	0·15	0·014	0·02	0·01	0·25	0·015
CaO	}0·007	}0·006	0·0020	0·004	0·0016	0·004	'Clear'
MgO			0·0012	0·0002	0·0003	0·004	
BaO	-	-	-	0·0015	Nil	-	
Cu	-	-	0·00004	-	0·00002	-	0·00005
Ni	-	-	0·00001	-	-	-	0·00002
Mn	-	-	0·0004	-	0·00003	-	0·00005
$NaClO_3$	-	-	-	0·30	Nil	-	'Low'

An examination of a 'very impure sodium hydroxide' has also been reported.[314] Purification of these products has been the subject of a number of patents.[315-318] Standards of purity of various grades of sodium hydroxide manufactured in the U.S.A. are published by the American Society for Testing Standards.[318a]

Sodium chloride can be removed by evaporating sodium hydroxide solutions until the salt precipitates.[319,320] Data on the solubility of sodium chloride in solutions of sodium hydroxide are available.[321] When most of the sodium chloride has settled and been removed cooling of the solution or further evaporation causes deposition of a hydrate of sodium hydroxide only slightly contaminated with salt.[322] By concentrating a solution under suitable conditions fine sodium chloride crystals and coarse sodium hydroxide monohydrate crystals can be deposited together and separated by filtration through a filter of the right porosity.[323] A similar separation can be effected between fine sodium chloride and coarse crystals of $2NaOH,7H_2O$.[324] Concentration at temperatures around 10°C. results in deposition of $2NaOH,7H_2O$,[325-327] while concentration at about 60°C. yields $NaOH,H_2O$,[328,329] both substantially pure.

The system Na_2SO_4-Na_2CO_3-NaCl-NaOH-H_2O has been studied and it has been found that the sodium chloride content of commercial sodium hydroxide solutions can be reduced to 0·1% by the addition of sodium carbonate and sodium sulphate to the solution at about 100°C. followed by filtration and removal of sodium chloride at about 50°C.[330] Recovery of sodium chloride containing less than 1% of sodium sulphate and suitable for recirculation to diaphragm cells has also resulted from studies on this system.[331] This use of sodium sulphate to remove sodium chloride from sodium hydroxide has been established for many years.[332-336] In one process the sodium hydroxide solution is filtered through a layer of sodium sulphate at 140°C. and then cooled to room temperature. The sodium chloride forms a precipitate and the concentration in the solution is reduced to about 0·2%. Sodium carbonate is partially removed at the same time.[337] Other sulphates and sulphuric acid itself have also been recommended for this purpose.[338,339] Magnesium or calcium compounds have been used along with the sodium sulphate; they reappear when the sodium hydroxide is subsequently cooled and traces of iron are removed with the sodium chloride.[340] The removal of the sodium chloride is the result of the formation of a slightly soluble triple salt of the composition $NaOH,NaCl,Na_2SO_4$.[341] The sodium hydroxide and sodium chloride in this salt can be dissolved in a little water and a residue of most of the sulphate is left which can be used again.[342-344] Sodium carbonate can be used instead of the sulphate.[345]

The removal of chlorate to render the sodium hydroxide suitable for use in the viscose rayon industry can be achieved by dispersing Raney nickel in a 50% solution of sodium hydroxide which is then heated to 165°C. in hydrogen at a pressure of 165 lb. per sq. in. The sodium chloride formed is insoluble in the sodium hydroxide and is removed with the catalyst by filtration. Contamination of the sodium hydroxide with nickel is negligible.[346] Chlorate can be removed by reduction with sodium sulphite at temperatures above 100°C.[346a] Sucrose is yet another reducing agent effective in removing chlorate.[285a,346b] An electrolytic reduction method of converting chlorate to chloride is also employed.[347]

Sodium sulphate can be deposited when solutions of sodium hydroxide are concentrated above 50°C. and then cooled to this temperature.[348,349] It is also removed by treating hydroxide solutions with carbon dioxide or carbonates. A precipitate containing sodium sulphate and sodium carbonate is obtained, and the solution can be filtered through a filter bed consisting of solid sodium carbonate and calcium carbonate.[350] The existence of a double salt of variable composition $(1{\cdot}4–2{\cdot}2)Na_2SO_4,Na_2CO_3$ has been demonstrated from studies of the system Na_2CO_3-Na_2SO_4-$NaOH$-H_2O.[351]

Sodium carbonate can be removed by adding an excess of calcium carbonate and if necessary seeding with crystals of the double salt $Na_2CO_3,CaCO_3$. A precipitate of the latter is obtained. Further purification can be effected by adding strontium or barium peroxide.[352,353] Cooling solutions obtained from the lime-soda process to temperatures below 0 °C. causes separation of solid sodium carbonate decahydrate. In this way the sodium carbonate content of solutions can be reduced to less than 1%.[354,355] Other ways of making carbonate-free alkali are described by Kolthoff.[356]

Silica is removed by adding calcium or magnesium hydroxide[357] or strontium sulphate.[358] The latter can also be used to eliminate alumina and iron. To purify 50% hydroxide solutions from iron, agitation of the solution with its own sludge is proposed.[359] The principal method of obtaining iron-free sodium hydroxide solutions appears to be that in which a magnesium salt, oxide or hydroxide is added to the solution.[340,360,361] Other alkaline earth compounds are also effective, and it has been recommended that the lime-soda process be carried out with a lime obtained from dolomite. Treatment of sodium hydroxide solution with sodium hypochlorite and manganese dioxide reduces both the iron and the manganese contents of the solution.[362a]

Interesting methods of purifying sodium hydroxide involve the use of ammonia. There are two processes, one being a liquid-liquid extraction process. Ammonia is added to an aqueous solution containing over 20% of sodium hydroxide at about 60°C. until two liquid layers are formed, the lower containing a greater concentration of sodium hydroxide.[363] The more modern

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counter-current techniques of liquid-liquid extraction are adaptable to this process. Ammonia of about 70–90% concentration is pumped against a current of sodium hydroxide solution. Sodium chloride can be reduced to about 0·1% or less, and sodium chlorate in diaphragm cell liquors can be reduced to zero. The concentration of the ammonia solution determines the concentration of the purified sodium hydroxide solution which may be much higher than that of the feed. Residual ammonia can be removed from the pure sodium hydroxide solution by evaporating it under reduced pressure or by blowing air through it.[364,365] In the second process ammonia is added to a more concentrated sodium hydroxide solution, preferably one containing more than 40% of sodium hydroxide, at a lower temperature, 25°C. or less. A second liquid phase does not then form. A precipitate of a sodium hydroxide hydrate is obtained.[366-368] Any sodium chloride originally present is retained in the solution.[369] A combination of both processes has been recommended. Ammonia solution is mixed with sodium hydroxide solution at 45–60°C. until two liquid layers are formed, and then more ammonia is added while the solutions are cooled. The two liquid layers merge into one and solid sodium hydroxide hydrate which contains about 64–68% of sodium hydroxide contaminated with very little sodium chloride is precipitated.[370,371] A modification of the ammonia process is effective in removing silica from sodium hydroxide solutions. By maintaining a suitable temperature and a high pressure of ammonia separation of liquid phases and of a sodium hydroxide precipitate is prevented, but a precipitate of silica is obtained instead.[372]

Electrolytic caustic soda solutions, especially from diaphragm cells, are frequently discoloured, and the solid sodium hydroxide obtained on evaporation is blackened. A crystalline organic compound, which may be the cause of this colour in some solutions, has been isolated from old graphite anodes. It has the empirical formula $C_{10}H_5O_9Cl$. It may be pyromellitic acid chloroquinone, and it is probably a result of oxidation of the anode.[373] The blue colour in liquor from diaphragm cells of the Allen-Moore type has been attributed to the presence of sodium ferrate introduced from the cathode as a result of oxidation by sodium chlorate formed in the electrolysis. The colour is discharged by adding hydrogen peroxide or sodium hypochlorite.[374] However, similar blue colours have been removed from commercial liquors by the *addition* of a small quantity of sodium ferrate followed by washing.[375] Heating at high pressures[376] and electrical coagulating methods[377] also remove these colours. A green colour attributed to manganic products has been observed in liquors from the lime-soda process and can be removed by treating the solution with zinc. A colloidally dispersed solid which is collected on an adsorbent is formed.[378]

Waste sodium hydroxide solutions from viscose rayon manufacture are contaminated with colloidal organic substances. These are removed by dialysis procedures.[379,380] Volcanic stone[381] or mercerized fabrics are used as diaphragms.[382-386]

Very pure sodium hydroxide can be made by extraction from an impure aqueous solution into an immiscible alcoholic solution. Alcohols containing more than two carbon atoms per molecule are suitable.[387] Carbonate-free sodium hydroxide solution is easily made in the laboratory by adding small pieces of sodium to water on which is a layer 3–4 cm. thick of ether which prevents absorption of carbon dioxide during the preparation.[388] Other preparations of carbonate-free sodium hydroxide have been described.[356,389] Pure sodium hydroxide can be prepared by repeated crystallization from water.[389a] The separation of potassium and sodium hydroxides is achieved by fractional crystallization. Concentration of solutions at temperatures above 40°C. causes crystallization first of potassium hydroxide; sodium hydroxide is then deposited by further concentrating at a lower temperature.[390-392]

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THE PHYSICAL PROPERTIES OF SODIUM HYDROXIDE

Anhydrous Sodium Hydroxide

Several values of the specific gravity of sodium hydroxide are given in Mellor, II, 500; these range from 1·723 to 2·130. The latest value for the density at 25°C. is 2·02, and this is also the value calculated from *X*-ray crystallographic data.[1,2] The density of molten sodium hydroxide between 320°C. and 450°C. lies between 1·786 and 1·722g. per c.c.; the values can be represented by the equation:-

$$d_t = 1{\cdot}746\,[1 - 2{\cdot}74 \times 10^{-4}(t - 400)].$$

At higher temperatures, from 690°C. to 920°C., the density can be represented by the equation:-

$$d = 1{\cdot}94 - 0{\cdot}00047t.$$

Sodium carbonate causes an increase in the density of molten sodium hydroxide at all temperatures in the range 320°C. to 450°C.[3-6]

The melting point has been frequently redetermined and there seems to be general agreement on a value of 322°C., though others have been reported including one as high as 327·6°C.[7-11] One of the chief difficulties encountered in these determinations has been the presence of impurities, principally water and sodium carbonate. To overcome this difficulty measurements have been made with sodium hydroxide containing known amounts of these impurities and the results extrapolated to zero impurity. Many of the measurements of other properties quoted later in this section have been made in the same way. The melting point of sodium hydroxide is reduced by the addition of sodium carbonate until a eutectic is formed at 22wt.-% of sodium carbonate, which melts at 286°C.[8] The following equation relates the melting point of sodium hydroxide to the proportions of sodium carbonate and water present in the material:-

$$t = 327{\cdot}6 - 0{\cdot}196p - 0{\cdot}0011p^2 - 0{\cdot}30w,$$

where p = wt. in g. of sodium carbonate in 1000g. of the sample, and w = wt. in g. of water in 1000g. of the sample.[11] Since the term 327·6 refers to the melting point of pure sodium hydroxide and is more than 5° higher than the value most generally accepted, the above equation may be of doubtful validity. Studies of the systems NaCl-NaOH and NaCl-NaOH-H_2O show that the m.p. of sodium hydroxide is raised by the addition of sodium chloride.[7,12] The system NaOH-KOH has a eutectic point at 50mol.-% at 170°C.[13] The systems NaOH-NaBr, NaOH-NaI, and NaOH-NaBr-NaI have also been studied.[14] The boiling point of sodium hydroxide has been found to be 1388°C.[7]

Sodium hydroxide exists in two crystalline forms. Several values have been found for the transition temperature, the highest being 299·6°C., quoted in Mellor, II, 500.[7-9,11,15,16] The transition appears to be very sensitive to pressure changes; transition temperatures of 280·4°C. in an inert atmosphere and 287·3°C. in a vacuum have been found by the same workers. The high-temperature, or β-form, has been reported as melting at 283·6°C. in an inert atmosphere and at 304·3°C. in a vacuum.[17] Since both these figures are below the usually accepted values of the m.p. of sodium hydroxide, they would appear to be somewhat uncertain. The heat of transition has been given as 158·9 abs. joules per g.; the same value has been found for the latent heat of fusion, though it has also been reported that the heat of transition is greater than the heat of fusion.[8,9,15]

The low-temperature, or α-, form of sodium hydroxide has an unusual crystal structure possessed by very few substances, α-potassium hydroxide being one. The structure is orthorhombic, having the space-group *Cmcm*; the lattice constants are $a = b = 3{\cdot}39_7 \pm 0{\cdot}03$A., $c = 11{\cdot}3_2 \pm 0{\cdot}05$A., and there are four formula units per unit cell. Each sodium ion has five nearest hydroxyl ion neighbours at five of the corners of an octahedron and at a distance of 2·4A. A layer structure results somewhat intermediate in form between the six-co-ordination structure of magnesium hydroxide and the four-co-ordination structure of lithium hydroxide. It has been suggested, however, that the subject requires re-examination.[2,18-20] The positions of hydrogen atoms have also been located by means of infra-red and Raman spectra; from these results it appears that there is no hydrogen bonding.[21] X-Ray analysis has shown the structure of β-sodium hydroxide to be cubic, but no details have been given.[17]

Detailed X-ray crystallographic studies of the hydrates of sodium hydroxide have shown the formation of ten different hydrates. The structural data for these are given in Table V.

TABLE V.- CRYSTAL STRUCTURES OF THE HYDRATES OF SODIUM HYDROXIDE

Hydrate	Crystal System	Space Group	Lattice Constants, A.	Formula Units per Unit cell
$NaOH,\frac{1}{2}H_2O$				
$NaOH,H_2O$	orthorhombic	$Pcab$	$a = 6{\cdot}21$, $b = 11{\cdot}72$, $c = 6{\cdot}05$	8
α-$NaOH,2\frac{1}{2}H_2O$	orthorhombic	$P2_12_12_1$	$a = 12{\cdot}48$, $b = 13{\cdot}50$, $c = 6{\cdot}27$	4
β-$NaOH,2\frac{1}{2}H_2O$	probably orthorhombic			
$NaOH,2\frac{3}{4}H_2O$	monoclinic	Aa or $A2/a$	$a = 23{\cdot}55$, $b = 6{\cdot}44$, $c = 22{\cdot}19$ $\beta = 114^\circ 12'$	4 or 8
$NaOH,3\frac{1}{10}H_2O$	orthorhombic	$Pb2a$ or $Pbma$	$a = 50{\cdot}00$, $b = 13{\cdot}32$, $c = 6{\cdot}25$	4 or 8
$NaOH,3\frac{1}{2}H_2O$	monoclinic	$P2_1/a$	$a = 11{\cdot}64$, $b = 12{\cdot}38$, $c = 6{\cdot}49$ $\beta = 104^\circ 7'$	4
$NaOH,4H_2O$	monoclinic	$C2/m$	$a = 15{\cdot}45$, $b = 4{\cdot}05$, $c = 9{\cdot}43$ $\beta = 110^\circ 50'$	4
$NaOH,5H_2O$	monoclinic	$P2_1/n$	$a = 15{\cdot}78$, $b = 25{\cdot}22$, $c = 12{\cdot}90$ $\beta = 102^\circ 18'$	4
$NaOH,7H_2O$	monoclinic	$P2_1/c$	$a = 7{\cdot}34$, $b = 16{\cdot}41$, $c = 6{\cdot}90$ $\beta = 92^\circ 53'$	4

Hydrate	X-Ray Density	Measured Density	Reference
$NaOH,\frac{1}{2}H_2O$			22
$NaOH,H_2O$	1·72	1·74	23,24
α-$NaOH,2\frac{1}{2}H_2O$	1·61	1·61(-50°C.)	23
β-$NaOH,2\frac{1}{2}H_2O$			23
$NaOH,2\frac{3}{4}H_2O$	1·55	1·56(-103°C.)	23
$NaOH,3\frac{1}{10}H_2O$	1·53	1·52(-42°C.)	23
$NaOH,3\frac{1}{2}H_2O$	1·51	1·50(-70°C.)	23
$NaOH,4H_2O$	1·41	1·41(-80°C.)	23 25-29
$NaOH,5H_2O$	1·38	1·38(-60°C.)	23
$NaOH,7H_2O$	1·33	1·30(-52°C.)	23,30

Most of the hydrates in Table V correspond to those originally reported by Pickering (1890) in his study of the solubility of sodium hydroxide. The hydrates then reported are:- $NaOH,H_2O$; $NaOH,2H_2O$; $NaOH,3H_2O$; (or possibly $NaOH,3{\cdot}1H_2O$); $NaOH,3{\cdot}5H_2O$; α-$NaOH,4H_2O$; β-$NaOH,4H_2O$; $NaOH,5H_2O$; $NaOH,7H_2O$. (See Mellor, II, 502).

$NaOH,H_2O$ has a layer structure; within each layer there is a system of co-ordination bonds and strong hydrogen bonds (at 2·64–2·66A.), while weak hydrogen bonds at 3·11A. link successive layers.[24] The tetrahydrate crystallizes as thin sheets which melt at approximately −5°C. In the monoclinic structure each Na^+ ion is surrounded by five OH^- ions at a distance of 2·36A., and hydrogen bonds make up a three-dimensional network.[23,25-29]

The lattice energy of sodium hydroxide is 202kg.-cal. per g.-mol. at 0°C., this value being calculated for a rock-salt structure. The hydration energy is 210kg.-cal. per g.-mol. Corresponding data for the other alkali metal hydroxides are reported.[31,32] Heat capacity data, density, and the coefficient of cubical expansion have been used to calculate a quantity known as the cohesion pressure for the alkali metal hydroxides:-[33] [$K_{cr} = 0{\cdot}5C_{cr}(d_0/\beta_t)$, where C_{cr} = heat capacity, d_0 = density at °C., β_t = coefficient of thermal expansion].

The viscosity of molten sodium hydroxide over the temperature range 350–550°C. is given in Table VI.[5]

TABLE VI. - VISCOSITY OF SODIUM HYDROXIDE

Temp. °C.	Viscosity, poises
350	0·040
400	0·028
450	0·022
500	0·018
550	0·015

Sodium carbonate has a very small effect on the viscosity but tends slightly to lower it; at 350°C. sodium hydroxide containing 18·6% of sodium carbonate has a viscosity of 0·0388 poise.[5] An expression relating viscosity, η, equivalent conductivity, λ, and molecular weight, M, *i.e.* $\frac{\lambda\eta}{M}$, has a constant value for a number of molten compounds, including sodium hydroxide, when measurements are made at the melting point of the substance.[34]

The specific heat of sodium hydroxide has been measured over a wide range of temperature from 60°K. to 1000°K. Values are summarized in Table VII.

TABLE VII. - SPECIFIC HEAT OF SODIUM HYDROXIDE

Temp. °K.	C_p g.-cal. per degree per g.-mol.	Reference
60	2·075	35
150	9·870	
250	13·25	
298·16	14·21	
298·2	14·26	16
350	14·77	
450	16·62	
550	19·60	

continued on following page

TABLE VII (continued)

Temp. °K.	C_p g.-cal. per degree per g.-mol.	Reference
α-NaOH 566·0	20·18	16
β-NaOH 566·0	20·56	
β-NaOH 592·3	20·56	
liquid NaOH 592·3	20·58	
650	20·50	
800	20·29	
1000	20·01	

An average value of 15·12g.-cal. per degree per g.-mol. over the temperature range 292–373°K. has also been reported.[36] Some of the above data have been embodied in equations of the usual type:-

for α-NaOH above 0°C. $C_p = 1{\cdot}476 + 4{\cdot}39(10^{-4})t + 5{\cdot}90(10^{-6})t^2$;

for liquid NaOH $C_p = 2{\cdot}199 - 1{\cdot}46(10^{-4})t$.

These equations give values for the specific heat in absolute joules per gram per degree C.[16] Data have also been obtained on the effect of sodium carbonate on the specific heat of molten sodium hydroxide.[37] Equations for the heat content of sodium hydroxide have been calculated from the above data on heat capacity:-[16]

for α-NaOH $H_t - H_o = 1{\cdot}4764t + (2{\cdot}195 \times 10^{-4})t^2 + (1{\cdot}968 \times 10^{-6})t^3$ abs. joules per g.;

for β-NaOH $H_t(\beta) - H_0(\alpha) = 29{\cdot}9 + 2{\cdot}15t$ abs. joules per g.;

for liquid NaOH $H_t(\mathrm{l}) - H_0(\alpha) = 180{\cdot}6 + 2{\cdot}1990t - (7{\cdot}31 \times 10^{-5})t^2$ abs. joules per g.

The heat of formation of sodium hydroxide from its elements has been found from electrochemical data and from heats of reaction. The e.m.f. of the cell sodium amalgam (0·207%)/saturated NaOH,H_2O,HgO/Hg has been measured and its dependence on temperature found. A value of −102·4kg.-cal. per g.-mol. is reported for ΔH_{298}.[38,39] A somewhat higher value, −112·4kg.-cal. per g.-mol., has been calculated from the heat of reaction of sodium with water.[40] The free energy of formation of sodium hydroxide, ΔF_{298}, has been evaluated from the data obtained with the cell incorporating NaOH,H_2O and has been found to be −90·76kg.-cal. per g.-mol.[38,39] A series of values of free energy of molten sodium hydroxide has been found from measurements on the polarization potentials of sodium hydroxide; they decrease from 53·62kg.-cal. per g.-mol. at 400°C. to 43·5kg.-cal. per g.-mol. at 700°C.[41] The entropy of sodium hydroxide is summarized in Table VIII.

More complete data are available in these two sources, and other values of the entropy of sodium hydroxide are reported elsewhere.[38,39,42]

The heat of vaporization of sodium hydroxide has been calculated from vapour pressure measurements between 1000°C. and the b.p., and a value of 31·5kg.-cal. per g.-mol. in the region of the b.p. has been found. The vapour pressure in this temperature range can be represented[43] by the equation:-

$$\log_{10} P\mathrm{atm.} = -31{,}500/4{\cdot}57T + 4{\cdot}1514.$$

Sodium hydroxide volatilizes appreciably in steam, the concentration of sodium hydroxide in the vapour increasing with the total pressure. The mixture of the vapours of sodium hydroxide and water shows no appreciable electrical conductivity.[44,45] The molar water content of molten sodium hydroxide

TABLE VIII. - ABSOLUTE ENTROPY OF SODIUM HYDROXIDE

Temp. °K.	S_T g.-cal. per degree per g.-mol.	Reference
60	1·16	35
150	7·01	
298·16	15·34	
298·2	15·34	16
350	17·66	
α-NaOH 566·0	25·75	
β-NaOH 566·0	28·43	
β-NaOH 592·3	29·37	
liquid NaOH 592·3	31·93	
700	35·36	
1000	42·57	

depends on the pressure of aqueous vapour in contact with the melt.[46] The pressure of water vapour in equilibrium with sodium hydroxide is affected by the presence of sodium carbonate and sodium chloride in the solid. Measurements of these water vapour pressures at 300°C. to 400°C. have been made and the results used to calculate the heat of absorption of water by molten sodium hydroxide.[47] A mixture of 84·5% NaOH, 15% Na_2CO_3 and 0·5% NaCl on absorption of 1·5% of water showed a heat of absorption of 12·9 kg.-cal. per g.-mol. in the temperature range 301°C. to 358°C.[47]

The electrical conductivity of molten sodium hydroxide has been measured at temperatures from the melting point to nearly 500°C.[48] The data in Table IX were obtained from measurements made with impure samples of sodium hydroxide containing known amounts of sodium chloride and sodium carbonate, the experimental results having then been extrapolated to pure sodium hydroxide.[4,5]

TABLE IX. - SPECIFIC CONDUCTIVITY OF MOLTEN SODIUM HYDROXIDE

Temp. °C.	Specific Conductivity mhos cm.$^{-1}$	Equivalent Conductivity
320	2·12	47·4
350	2·38	53·8
400	2·82	64·6
450	3·27	76·0

Temperature Coefficient: 0·00412 per °C.

The dependence of specific conductivity on temperature is given by the equation:-

$$\chi_t = 2\cdot82\,[1 + 3\cdot19 \times 10^{-3}(t - 400)]$$

where temperature is in °C.[5] The effects of the principal impurities likely to be found in sodium hydroxide on its conductivity are summarized in Figs. 1 and 2.[5]

Decomposition potentials of molten sodium hydroxide are given in Table X.

The decomposition potentials of several metal oxides dissolved in molten sodium hydroxide have also been found.[49] Table XI shows voltages of a number of cells incorporating molten sodium hydroxide and metal electrodes.[49]

The potentials of silver, copper, nickel, cobalt and tungsten given in Table XII have also been measured in molten sodium hydroxide with gold as

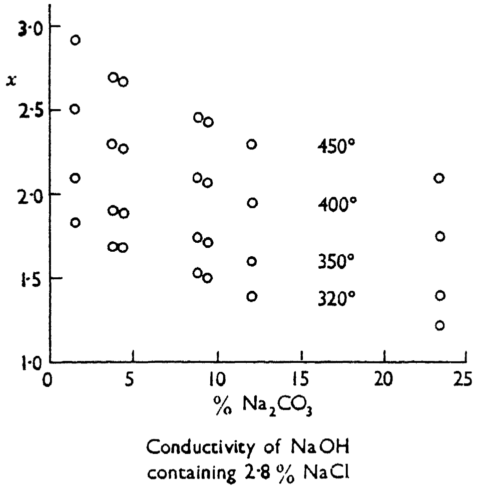

FIG. 1. CONDUCTIVITY OF NaOH CONTAINING 2·8% OF NaCl

the reference electrode.[51]

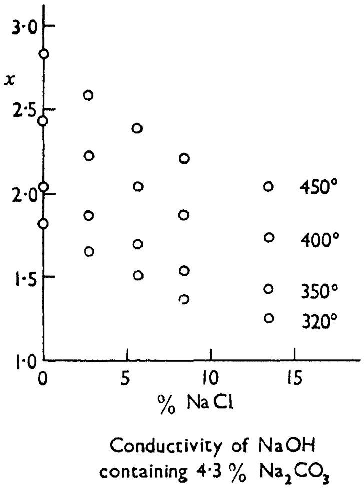

FIG. 2. CONDUCTIVITY OF NaOH CONTAINING 4·3% OF Na_2CO_3

TABLE X. - DECOMPOSITION POTENTIALS OF SODIUM HYDROXIDE

Temp. °C.	Decomposition Potential, volts	Reference
320	2·332	48
350	2·05	49
450	1·9	49
480	1·952	48
	2·32	50

TABLE XI. - E.M.F. OF MOLTEN SODIUM HYDROXIDE CELLS

Cell	e.m.f. (volts)
Zn/NaOH/Ni	1·4
Sn/NaOH/Ni	1·15
Sb/NaOH/Ni	1·05
Cd/NaOH/Ni	1·00
Pb/NaOH/Ni	0·80
Bi/NaOH/Ni	0·45
Pb/NaOH/Bi	0·35
Zn/NaOH/Cd	0·35

TABLE XII. - POTENTIALS OF METALS RELATIVE TO GOLD IN MOLTEN SODIUM HYDROXIDE AT 400°C.

Copper	+0·61V.
Nickel	+0·67V.
Silver	+0·68V.
Cobalt	+0·70V.
Tungsten	+1·05V.

Changes in the potential of these metals with time have been observed and have been attributed to the formation of a film on the electrode or to the dissolution of the metal in the melt, though below 400°C. none of the metals dissolved in sodium hydroxide to any appreciable extent in the absence of oxygen. The potential of silver in sodium hydroxide is more sensitive than that of other metals to low concentrations of impurities in the melt.

Measurements of oxygen overpotential on nickel and platinum electrodes in molten sodium hydroxide show that it is not of the same kind as that observed in the deposition of hydroxyl ions in aqueous solutions but is due to the change in concentration of the water in the melt in the immediate vicinity of the electrode. Traces of water are normally present in molten sodium hydroxide and more water is produced by the anode reaction. The overpotential has a low temperature coefficient and is independent of the nature of the electrode.[52,53] A study of the "anode effect", *i.e.* the disturbance which occurs at the anode during the electrolysis of molten electrolytes, has been made with a number of systems including sodium hydroxide. The effect occurs on carbon electrodes at a current density of 20amp. per sq.cm. with molten sodium and potassium hydroxides but at lower current densities with molten halides.[54] The electrode material is considered to be of great importance in the electrolysis of molten sodium hydroxide.[55] Under certain conditions, electrolysis of molten sodium hydroxide with an iron cathode leads to cathodic corrosion and deposition of sodium ferrite at the anode, an effect which has been explained by the formation of $FeOOH^-$ ions.[56] The electric discharge which occurs on the surface of molten sodium hydroxide in the region of the cathode has also been studied.[57]

When a potential difference of 10,000 volts is established between the surface of molten sodium hydroxide at 330°C. and a cathode of ferronickel, and a current of 20 milliamps passed at atmospheric pressure a steady, sparkless discharge takes place. With higher currents a spark discharge is established, and pulverization of the sodium hydroxide surface occurs.[57]

The refractive indices[58] of anhydrous sodium hydroxide and of the monohydrate are:-

NaOH, blades and plates flattened parallel to (001):	$\alpha = 1{\cdot}45_7$; $\beta = 1{\cdot}47_0$; $\gamma = 1{\cdot}47_2$
$NaOH,H_2O$:	$\alpha = 1{\cdot}435$; $\beta = 1{\cdot}470$; $\gamma = 1{\cdot}475$.

Measurements of the refractive index of molten sodium hydroxide at temperatures from the melting point to 440°C. vary linearly with temperature according to the equation:-

$$n = a - b \times 10^{-4}T.$$

Molecular refraction however is almost independent of temperature and is 5.47, the theoretical value for unionized sodium hydroxide being 5·37 and for ionized sodium hydroxide 5·03.[3, 59] The Raman spectrum of sodium hydroxide has been examined.[60] In the infra-red spectrum of powdered anhydrous sodium hydroxide bands at 6·0μ and 12·0μ have been observed, and another at 2·94μ has been attributed to the O – H linkage.[61] Photoluminescence of sodium and potassium hydroxide has been found to be due to the presence of small amounts of formate which changes partly to carbonate and oxalate when heated.[62]

Summaries of the properties of sodium hydroxide, especially thermodynamic properties,[42] thermal conductivities,[63] and properties of particular interest to technical users of sodium hydroxide,[64] have been published.

Physical Properties of Solutions of Sodium Hydroxide

Solubility in water

The solubility data previously reported (Mellor, II, 502) have recently been extended to higher concentrations of sodium hydroxide, and the phase diagram for the system has been completed (Fig. 3).[65]

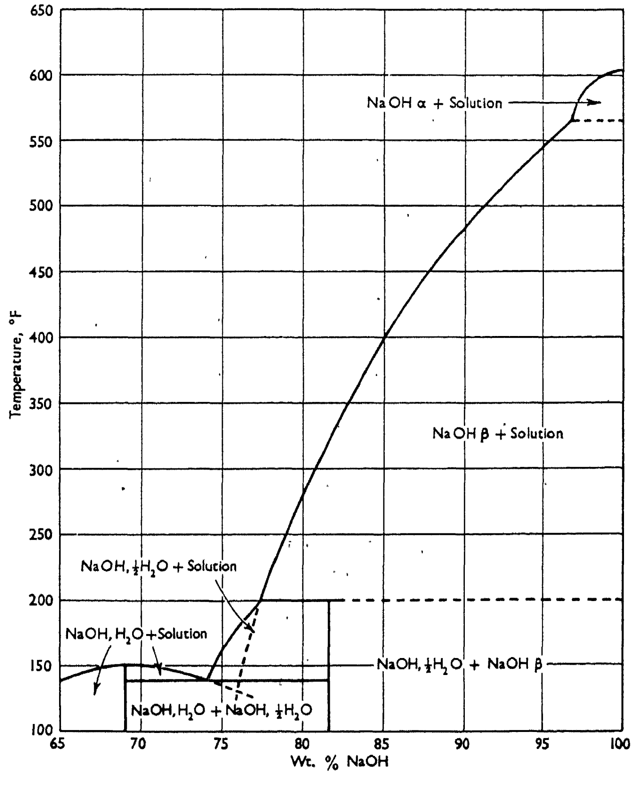

FIG. 3. PHASE DIAGRAM, NaOH-H_2O

The slight inflexion in the solubility curve at about 200°F. has been attributed to the separation of the hemihydrate, $2NaOH,H_2O$, first noted by de Forcrand (1901) and since detected by X-ray analysis.[22] (See page 671).

The effect of other solutes on the solubility of sodium hydroxide has been observed in a number of examinations of three-component systems: sodium carbonate-sodium hydroxide-water;[58] sodium sulphite-sodium hydroxide-water;[66] sodium tartrate-sodium hydroxide-water.[67-69] The influence of sodium hydroxide on the hydrothermal and pneumatalytic crystallization of minerals has been studied.[70,71]

Density

Many determinations have been made of the densities of sodium hydroxide solutions,[72-79] the values at 20°C. being listed in Table XIII.[79]

TABLE XIII.-DENSITY OF AQUEOUS SODIUM HYDROXIDE SOLUTION AT 20°C.

Wt.-% of NaOH	Molality of NaOH	Density
0	0·0000	0·99800
2	0·5101	1·02022
4	1·0415	1·04207
6	1·5955	1·06390
10	2·7774	1·10773
14	4·0693	1·15192
20	6·2492	1·21844
30	10·7129	1·32612
40	16·6646	1·43215
50	24·9969	1·52142

Density is a linear function of temperature, the temperature coefficient, α, being given by the equation:-

$$\alpha = 0{\cdot}0005 + 4{\cdot}9 \times 10^{-6}x,$$

where x is the wt.-% of sodium hydroxide. For many technical purposes the density of solutions containing 10% to 70% of sodium hydroxide in the temperature range 15°C. to 70°C. is given by:-

$$\alpha = 1{\cdot}02 + 0{\cdot}0105x - \alpha t,$$

α being the temperature coefficient and x the wt.-% of sodium hydroxide.[80] The effect of sodium carbonate and sodium chloride on the density of sodium hydroxide solution has been investigated.[74,76] The apparent partial molar volume of sodium hydroxide in aqueous solution has been calculated from densities of solutions; variations of this quantity with the concentration of the solution indicate structural changes in the solution, such as a change in the co-ordination number of the ions.[79] The density of solutions of sodium hydroxide in aqueous methanol has been measured; results are shown in Table XIV.[81]

TABLE XIV. - DENSITY OF SOLUTIONS OF SODIUM HYDROXIDE IN AQUEOUS METHANOL CONTAINING 9·889% OF METHANOL AT 25°C.

Molality	Density
0	0·980113
0·02252	0·981118
0·30000	0·993293
0·74971	1·012215

The volume changes that occur when sodium hydroxide is dissolved in water and when the solutions are diluted have been described in terms either of an increase in the volume of the system compared with that of the pure solvent or of a contraction compared with the sum of the volumes of the two components.[82,83] Volume changes have also been observed from measurements on the compressibility of sodium hydroxide solutions, and the results have been related to the hydration of the ions.[84,85] An ultrasonic method has been used to find the compressibility of sodium hydroxide solutions; results are given in Table XV.[75]

TABLE XV. - COMPRESSIBILITY COEFFICIENT, β, AND APPARENT MOLAL COMPRESSIBILITY, $\beta V-\beta_1 V_1$, OF SOLUTIONS OF SODIUM HYDROXIDE AT 25°C.

Normality	Density	$\beta \times 10^{-6}$atm.$^{-1}$	$(\beta V-\beta_1 V_1)\times 10^3$
2·2192	1·08670	31·23	−5·12
1·1081	1·04391	36·15	−5·85
0·5542	1·02114	39·12	−6·29

The compressibility coefficient of water at 25°C. is $42{\cdot}52 \times 10^{-6}$atm.$^{-1}$. The apparent molal compressibility has been found to be proportional to the square root of the concentration over a wide range of concentrations.[86]

Viscosity

The viscosity of sodium hydroxide solutions is given in Table XVI together with corresponding values of the density.[76]

TABLE XVI. - VISCOSITY AND DENSITY OF SODIUM HYDROXIDE SOLUTIONS AT 20°C.

Normality	Density (Corr. to *in vacuo*)	Viscosity (Centipoise)
1·109	1·0454	1·2621
1·888	1·0758	1·5067
2·990	1·1165	1·9604
4·677	1·1738	3·0508
6·032	1·2162	4·4132
8·309	1·2824	8·5511

The variation of viscosity with concentration at a constant temperature is also shown in Fig. 4.[87]

Several other determinations of viscosity have also been made.[72,74,77,88-93] Viscosity decreases regularly with temperature, though it has been reported that temperature has less effect on solutions of high concentration.[76,80] The viscosity of solutions of sodium hydroxide from 1 to 10N. and between 40°C. and 80°C. can be expressed by the formula:-

$$\mu = \mu_0 e^{\lambda K},$$

where μ is the viscosity at the concentration K, μ_0 is the viscosity of water, and λ is a constant.[94] Solutions of sodium hydroxide also obey the equation:-

$$\phi T^{3/2} = a_1 \exp.(b_1/T)$$

where ϕ is the fluidity of the solution at the absolute temperature T and a_1 and b_1 are constants.[95] The effect of sulphuric acid on the viscosity of sodium hydroxide solution has been studied; equimolecular quantities of sodium hydroxide and sulphuric acid give a minimum viscosity, and the neutralization of sodium hydroxide by sulphuric acid can be followed viscometrically.[96,97] The viscosity of a solution affects the rate of filtration of solids from it, and a study of this has been made with sodium hydroxide solutions.[98]

The diffusion of sodium hydroxide solutions from a capillary has been studied theoretically and experimentally.[99]

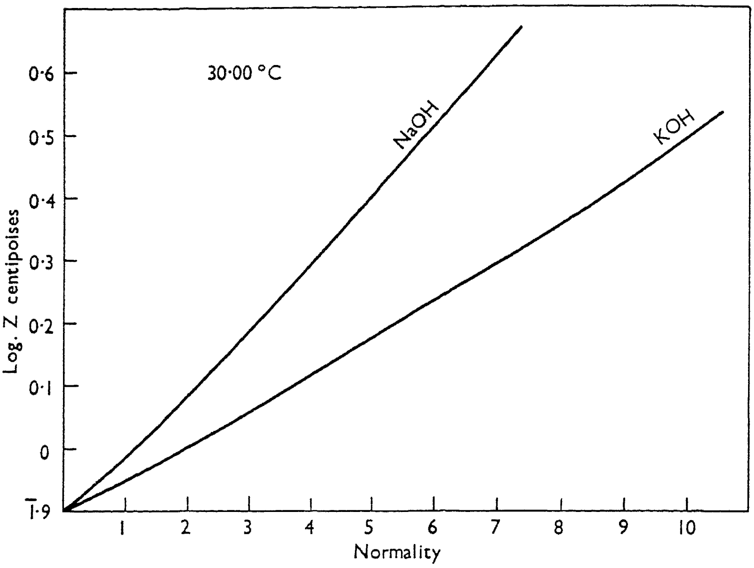

FIG. 4. VISCOSITY OF NaOH AND KOH SOLUTIONS AT 30°C.

Surface Tension.

The surface tension of solutions of sodium hydroxide is given in Table XVII.[88]

TABLE XVII.- SURFACE TENSION AND SPECIFIC GRAVITY OF SOLUTIONS OF SODIUM HYDROXIDE AT 20°C.

Normality	Wt.-% NaOH	Specific gravity	Surface tension dynes per cm.
0·257	1·02	1·011	73·4
1·31	5·00	1·0538	74·8
2·77	10·00	1·1089	77·0
6·09	20·00	1·2191	85·0

More recently the surface tension of a 1% sodium hydroxide solution has been found to be 71·24 dynes per cm.

The effect of wetting agents on the surface tension has been examined.[100] The contact angles of 1% sodium hydroxide solutions on iron, copper, brass and zinc surfaces coated with various materials have been measured.[101]

Thermal Conductivity.

A 10% solution of sodium hydroxide has a thermal conductivity of 0·539 kg.-cal. per metre hr. °C. The thermal conductivity increases with the concentration of the solution reaching a maximum with 40% of sodium hydroxide and then remaining constant.[102,103]

Osmotic Pressure and Related Properties.

Values of the osmotic pressure of sodium hydroxide solutions conform to the equation:-

$$P = P_{\text{calc.}} \times t_{\text{exp.}}/t_{\text{calc.}}$$

where $P_{\text{calc.}}$ is the osmotic pressure calculated for a non-electrolyte, and $t_{\text{exp.}}$ and $t_{\text{calc.}}$ are the experimental and calculated values of the depression of the freezing-point of the solution.[104] The osmotic pressures of some sodium hydroxide solutions are given in Table XVIII.[105]

TABLE XVIII.- OSMOTIC PRESSURE OF SODIUM HYDROXIDE SOLUTION

Temp. °C.	g. of NaOH per 100g. of water	Osmotic pressure atm.
30	10	154·9
	30	1081
45	10	153·3
	30	1119
60	10	164·0
	30	1073
70	10	182·0
	30	1059
80	10	173·0
	30	1052

Many determinations have been made of the vapour pressure of sodium hydroxide solutions.[106-115] The results in Table XIX were obtained by a method involving the saturation of air with the vapour of the solution.[105]

Other measurements of the vapour pressure of sodium hydroxide solutions are indicated in Fig. 5, where the vapour pressures of other solutions are included for comparison.[111]

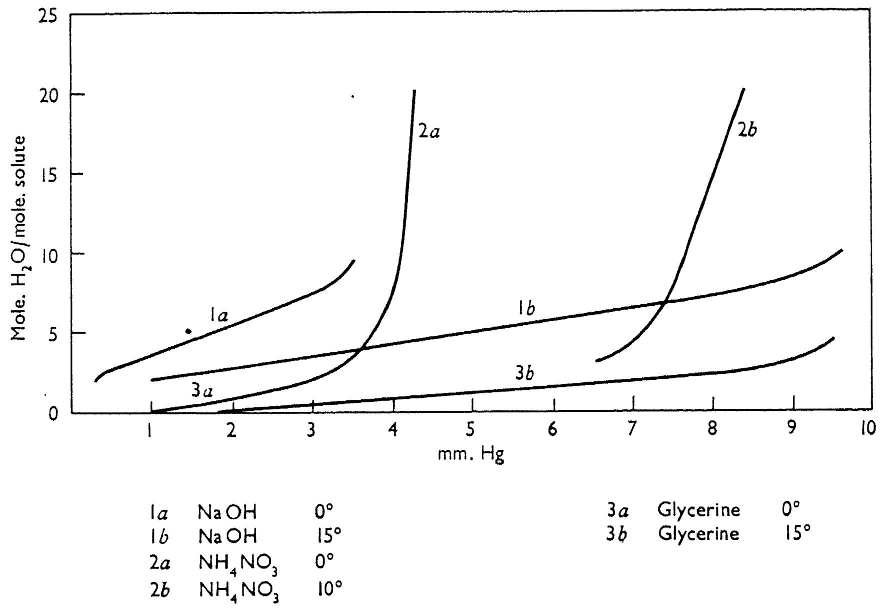

FIG. 5. VAPOUR PRESSURE OF SOLUTIONS

Accurate measurements of the vapour pressure of solutions have been made by the isopiestic method with results which are not always in agreement with those of the dynamic methods. A solution of sodium hydroxide at 25°C.

TABLE XIX. - VAPOUR PRESSURE OF SODIUM HYDROXIDE SOLUTIONS AT 30°C.

g. of NaOH per 100g. of soln.	Vapour pressure mm. of mercury
10	27·32
16·6	25·04
20	23·12
23	20·76
28	16·32
32	12·80
36	9·64
40	6·68
44	4·96
48	3·60

is allowed to come to equilibrium with water at a known lower temperature; the difference in the temperatures is measured potentiometrically, the solution and the solvent constituting half-cells.[116-118] Contamination of the solution with carbon dioxide causes a further lowering of the vapour pressure, and the extent of the lowering has been used to calculate the kinetics of the absorption of carbon dioxide by sodium hydroxide solution.[119]

The boiling points of sodium hydroxide solutions are indicated in Fig. 6.[120]

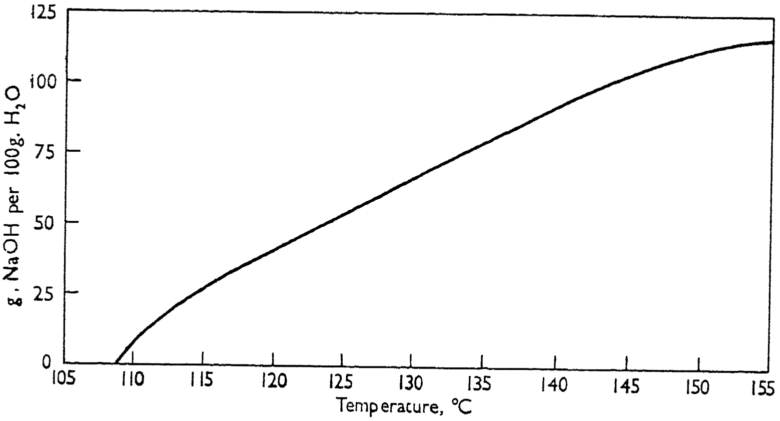

FIG. 6. BOILING POINT OF SODIUM HYDROXIDE SOLUTION

Reviews of boiling-points of sodium hydroxide solutions have been made.[65] The most probable values for concentrated solutions are given in Table XX.[121]

TABLE XX. - BOILING-POINTS OF CONCENTRATED SOLUTIONS OF SODIUM HYDROXIDE

Percentage of NaOH	Boiling-point °C.
50	145
60	185
70	240
80	312
90	640

Solutions of sodium hydroxide obey the Dühring and the Ramsay-Young boiling-point rules.[122-124] The mechanical loss of liquid during boiling has been studied, foam inhibitors being used in attempts to prevent such loss.[128] Freezing-point depression measurements have been made with sodium hydroxide dissolved in the ice-sodium nitrate eutectic.[126]

Heat of Solution and Specific Heat

Some of the results of vapour pressure measurements have been used to calculate the heats of dilution of sodium hydroxide solutions,[105,114] but this quantity has been more frequently determined directly by calorimetric methods.[127-135] Table XXI shows values of the heat of infinite dilution obtained with vapour pressure data,[105] and Table XXII shows values of the heat of partial dilution obtained calorimetrically.[134]

TABLE XXI.- HEAT OF DILUTION OF SODIUM HYDROXIDE SOLUTIONS

Initial Concn. (g./100g.)	Temp. °C.	Heat of Dilution kg.-cal.
30·0	20	28·5
	40	30·9
	60	31·0
27·5	20	19·5
	40	21·8
	60	22·8
25·0	20	12·7
	40	15·0
	60	16·7
20·0	20	4·3
	40	6·4
	60	7·5

TABLE XXII.- HEAT OF PARTIAL DILUTION OF SODIUM HYDROXIDE SOLUTION AT 20°C.

Square root of molality		ΔH_{20} (Joules per mole of NaOH)
Initial	Final	
1·4900	1·0536	461
1·4900	0·7451	767
1·4900	0·5268	889
1·4900	0·3726	902
1·4900	0·2634	860
1·4900	0·1863	803
1·4900	0·1317	749
1·4900	0·0000	682

The heat *evolved* is at a maximum when the solution is diluted from saturation to a concentration corresponding to $NaOH,17{\cdot}9H_2O$.[128] Data on heats of dilution of very dilute solutions have been used to find the heat of neutralization of sodium hydroxide; values of 13·60 and 13·65kg.-cal. per g.-mol. have been reported.[128,129,136,137] Values of the heats of dilution at various concentrations may afford evidence on the dissociation of sodium hydroxide and as to the extent of hydration of the ions.[127,130] Heats of solution of sodium hydroxide in dilute solution also afford a basis for the calculation of heats of hydration of the ions formed, from which the extent of hydration and the effective radius of the ions within the hydration shell have been found. At high dilution the hydration number of Na^+ ion is 6, and of the OH^- ion is 8; the effective ionic radius of the Na^+ ion within the hydration shell is 1·57A.

and of the OH^- ion is 1·68A.[138]

The heat of solution in concentrated solutions has been studied theoretically, and expressions have been derived for the calculation of heats of solution in systems that are not easy to deal with calorimetrically.[139] Measurements have been made of the heat of solution of sodium hydroxide in ethanol–water mixtures.[140]

TABLE XXIII.- HEAT OF SOLUTION OF SODIUM HYDROXIDE IN AQUEOUS ETHANOL AT 23°C.

Wt.-% of ethanol	Heat of solution kg.-cal. per mole of NaOH
0	10·00
10	9·60
20	9·09
30	8·65
40	8·74
50	9·01
60	9·52
70	9·73
93·8	10·74

When two parts of a liquid solution are maintained at different temperatures the solute will, in general, tend to migrate from the warmer to the colder region. This effect, known as the Soret effect, has been investigated for solutions of sodium hydroxide.[141]

Values of heats of dilution may be used for the calculation of specific heats and heat content of sodium hydroxide solutions; several experimental determinations of the specific heats have also been made.[73,127–129,131,135,142–150] Above 60°C. the specific heat of sodium hydroxide solution is almost independent of temperature, but there is considerable dependence at 0°C.[149] The dependence of specific heat on the consideration of the solution is indicated in Table XXIV.[147]

TABLE XXIV.- SPECIFIC HEAT OF SODIUM HYDROXIDE SOLUTION AT 25°C.

Molality per 1000g. of water	Specific heat g.-cal. per g.
0·0396	0·99747
0·0910	0·99457
0·1635	0·99021
0·2395	0·98635
0·4754	0·97457
0·9999	0·95261
1·8261	0·92683
2·5513	0·91041

The partial molal heat capacity of the solute $(\bar{C}p_2)$ in solutions of sodium hydroxide is given by the equation:-

$$(\bar{C}p_2) = -26{\cdot}59 + 26{\cdot}24\sqrt{m}$$

and the relative partial molal heat capacity of the solvent by:-

$$(\bar{C}p_1 - \bar{C}p_1^0) = -0{\cdot}1579m^{3/2}$$

where m is the molality of the solution.[147]

Many values of the heat content (enthalpy) of sodium hydroxide solutions have been derived from heats of dilution and specific heats, and a more detailed thermodynamic treatment of the data leads to values of the relative partial molal heat content of the water and of the sodium hydroxide.[131-135,143,148,151,152] Some results are given in Table XXV.[134]

TABLE XXV. - RELATIVE PARTIAL MOLAL HEAT CONTENT OF SODIUM HYDROXIDE ($\bar{L}_2$) AND WATER ($\bar{L}_1$) IN SODIUM HYDROXIDE AT 25°C.

Square root of molality	(International Joules per mole)	
	$\bar{L}_2$	$\bar{L}_1$
0·1000	+266	−0·0147
0·2000	+437	−0·0827
0·3000	+524	−0·177
0·4000	+557	−0·243
0·5000	+541	−0·177
0·6000	+469	+0·224
0·7000	+370	+0·983
0·8000	+252	+2·18
0·9000	+127	+3·84
1·0000	−18·1	+6·18
1·1000	−160	+9·00
1·2000	−270	+11·6
1·3000	−337	+13·5
1·4000	−363	+14·4
1·5000	−347	+13·7
1·6000	−293	+11·4
1·7000	−161	+4·85
1·8000	+53·7	−7·0
1·9000	+322	−23·7

Conductivity of Solutions of Sodium Hydroxide

Several measurements have been made of the electrical conductivity of sodium hydroxide solutions from which equivalent conductivities and ionic mobilies have been calculated.[74,89,151,153-163] Recent results of conductivity measurements are given in Table XXVI.[163]

TABLE XXVI. - SPECIFIC CONDUCTIVITY OF SODIUM HYDROXIDE SOLUTION AT 25°C.

g. of NaOH per 10^6g. of solution	Specific cond. mhos per cm. × 10^6	Equivalent conductivity
0	0·15	247·7 (= Λ_0)
1·5785	9·71	246·9
5·7950	35·61	246·6
14·142	86·61	245·8
29·265	178·49	244·8
50·768	308·20	243·6
111·30	669·45	241·4
224·58	1341·0	239·6

The specific conductivity of solutions of NaOD dissolved in deuterium oxide has also been determined. For concentrations similar to those in Table XXI the equivalent conductivity lies in the range 154–158mhos cm.$^{-1}$ The limiting values of the ionic conductances of the hydroxyl ion in ordinary water and of the OD$^-$ ion in heavy water have been calculated and are 197·6 and 119·0 respectively.[163] A study of the mobility of the proton in ice has been based on measurements of the conductivity of frozen solutions of sodium hydroxide and of other electrolytes.[164] The conductivity of sodium hydroxide solution with high frequency alternating currents has also been measured.[165-168]

The conductivity coefficients of sodium hydroxide in water and in various alcohols have been measured. This quantity is defined as the ratio of the measured equivalent conductance to the ideal value with complete ionization, and it is a measure of the dependence of ionic molality on concentration. Values are shown in Table XXVII.[169]

TABLE XXVII. - CONDUCTIVITY COEFFICIENTS (f_λ) OF SOLUTIONS OF SODIUM HYDROXIDE AT 25°C.

Solute	Litres containing 1g.-mol.	f_λ
Water Dielectric constant = 78·8	4 16 32 64 128 256	0·8356 0·7973 0·9180 0·9348 0·9483 0·9591
Methanol Dielectric constant = 33	32 64 128 256 512	0·686 0·748 0·800 0·843 0·876
Ethanol Dielectric constant = 25·4	32 64 128 256 512	0·492 0·572 0·655 0·725 0·791
n-Propanol Dielectric constant = 22·4	32 64 128 256 512	0·356 0·434 0·5195 0·6175 0·710

The effect of varying the pressure up to 200atm. during electrolysis of aqueous solutions has been examined.[170]

There is little pressure effect up to 100atm. at a current density of less than 2ma. per sq.mm. With higher pressures there is an increase in the conductivity of the solutions, which is followed at still higher pressures by a decrease.[170]

It has been suggested that there is little hydration of the cations in aqueous solutions of alkali metal hydroxides and therefore little interposition of water molecules between cations and anions. Consequently alkali metal hydroxides should be weaker electrolytes than other alkali metal compounds.[171]

The addition of aluminium hydroxide causes a decrease[172] in the conductivity of sodium hydroxide solutions owing to the formation of the less mobile aluminate ion, AlO_2^-. Small quantities of sodium silicate, such as might dissolve in sodium hydroxide solutions from glass vessels, affect the conductivity of solutions.[173] Changes in the conductivity of sodium hydroxide solutions are also caused by non-electrolytes and by colloidal substances such as gelatin, gums, salep, and dextrin.[174-178] Transport numbers of the sodium and hydroxyl ions have been calculated from e.m.f. measurements with concentration cells.[179,180] Results are shown in Table XXVIII.[180]

The pH of solutions of sodium hydroxide varies with the temperature according to a linear relationship, being lower at higher temperatures. Values of pH have been obtained by indicator methods and by measurements with

TABLE XXVIII.- TRANSFERENCE NUMBERS OF SODIUM HYDROXIDE AT 25°C.

Mols NaOH per kg. of water	N_c (Transference number of Na^+)
0·01004	0·203
0·01289	0·201
0·02578	0·195
0·0644	0·187
0·1288	0·182
0·2575	0·176
0·3717	0·173
0·9738	0·165
1·482	0·161
2·825	0·153

quinhydrone, hydrogen, and glass electrodes.[181-185] The pH decreases with rising temperature when the solution contains citrates in addition to the sodium hydroxide, but in the presence of glycine or borates the pH increases with rising temperature.[182,186] Sucrose lowers the pH of dilute sodium hydroxide solutions in accordance with the assumption that sucrose is a polybasic acid.[187] From e.m.f. measurements with a calomel electrode system the pH of concentrated alkali solutions has been calculated, and from the results it has been suggested that the sodium ion is more highly hydrated than the potassium ion in these solutions.[188] Activities and activity coefficients of the ions present in sodium hydroxide solutions have been measured by a variety of potentiometric methods and over a wide range of concentrations.[81,180,189-201] Collected data on activities have also been published, and some values are shown in Table XXIX.[202]

TABLE XXIX.- ACTIVITY COEFFICIENTS OF SODIUM HYDROXIDE IN AQUEOUS SOLUTION AT 25°C.

Concentration Moles per 1000g. of water	Activity Coefficient
0·1	0·766
0·2	0·727
0·3	0·708
0·4	0·697
0·5	0·690
0·6	0·685
0·7	0·681
0·8	0·679
0·9	0·678
1·0	0·678
1·2	0·681
1·4	0·686
1·6	0·692
1·8	0·700
2·0	0·709
2·5	0·743
3·0	0·784
3·5	0·835
4·0	0·903
4·5	0·985
5·0	1·077
5·5	1·181
6·0	1·299

Dissociation constants have been found for various sodium hydroxide solutions, and there is some evidence that in certain reactions involving sodium methoxide sodium hydroxide undergoes an acidic dissociation.[189,203,204]

Discharge potentials of sodium hydroxide solutions and overpotentials on copper and silver in sodium hydroxide solution have been measured.[205-207] With a platinum anode there are two anodic potentials in sodium hydroxide solution, at 1·00 and 1·40 volts.[207] The presence of vanadate ions during electrolysis of sodium hydroxide lowers the hydrogen overpotential.[208] Cathodic reduction in sodium hydroxide solution has been studied, and the mechanism of the release of hydrogen at cathode surfaces in sodium hydroxide solution has been followed by the Schlieren photographic method.[209 211]

Optical Properties of Sodium Hydroxide Solutions

The refractive index of sodium hydroxide solutions varies with the concentration, and the concentration of solutions can be measured accurately by means of an immersion refractometer. Results are shown in Table XXX.[212]

TABLE XXX. - REFRACTIVE INDEX OF SODIUM HYDROXIDE SOLUTION

Temperature	Normality	Refractive Index
20°C.	0	1·33302
	0·197	1·33517
	0·328	1·33660
	0·886	1·34236
	1·378	1·34714
	2·462	1·35685
	3·288	1·36364
25°C.	0	1·33251
	0·197	1·33467
	0·327	1·33605
	0·885	1·34174
	1·376	1·34644
	2·457	1·35603
	3·280	1·36279
30°C.	0	1·33196
	0·197	1·33411
	0·326	1·33551
	0·884	1·34108
	1·374	1·34572
	2·452	1·35530
	3·273	1·36204

Raman spectra are not usually observed with aqueous solutions containing only monatomic ions, and spectra observed with sodium hydroxide solutions are attributed to the hydroxyl ion with its O–H bond.[213-216] Results of light-scattering measurements with sodium hydroxide solutions indicate that a quasi-crystalline structure involving hydrogen bonds exists in concentrated solutions and that it is broken down on dilution.[217] The infra-red spectra of sodium hydroxide solutions also show bands due to the hydroxyl ion, but bands at 2·60μ and 1·81μ, thought to be characteristic of the undissociated sodium hydroxide molecule, have also been observed.[218,219] Microwave spectra of very dilute sodium hydroxide solutions have been compared with those of pure water. At 1 kilocycle in ice which is 0·0001N. to sodium hydroxide the Debye absorption (due to lattice defects in ice) and the ionic absorption are different from the absorption in water.[220] The effect of sodium hydroxide on the *X*-ray diffraction of water has also been examined.[221,222] There are two structural units in 38% sodium hydroxide solution; one consists of a sodium ion attached to one oxygen atom at a distance of 2·03A. in the tetrahedral arrangement of liquid water, and the other consists of a sodium ion surrounded tetrahedrally by four oxygen atoms also at a distance of 2·03A.[223,224] Sodium hydroxide and many other substances affect the fluorescence and thermoluminescence of ice exposed to γ-rays with results that provide information on the hydration of the cation.[225]

Dielectric and Magnetic Properties

Values of the dielectric constant of sodium hydroxide solutions have been used in studies of the structure of these solutions. The dielectric constant is independent of the frequency between 50 and 2200 cycles per sec.; it decreases at first with increasing concentration of the solution, passes through a minimum value, then increases rapidly with concentration, finally reaching a limiting value which is sometimes above that of pure water. Some values are given in Table XXXI.

TABLE XXXI.- DIELECTRIC CONSTANT OF SODIUM HYDROXIDE SOLUTION AT 50 CYCLES

Normality	Temp. °C.	Dielectric Constant
0	20·4	80·0
0·00250	20·8	74·9
0·00375	20·6	74·0
0·00500	22·2	79·2
0·00625	21·4	80·3
0·00750	21·8	81·4
0·01000	22·5	83·7
0·01250	22·2	85·0

The initial decrease is explained by the hydration of the ions which disturbs the orientation of the water molecules in the electric field; at higher concentrations of sodium hydroxide, hydration is less, and the water molecules are free to align themselves in the field.[226-229] The dielectric constants of emulsions of aqueous sodium hydroxide with oils have also been measured, and results are shown in Table XXXII.[230,231]

TABLE XXXII.- DIELECTRIC CONSTANT OF EMULSIONS OF 0·5N. NaOH WITH TRANSFORMER OIL

Concentration of NaOH solution vol.-%	Dielectric Constant
2·5	2·40
5·0	2·56
7·5	2·80
10·0	3·00

The movement of the emulsion has no effect on the dielectric constant

The Faraday effect (the magnetic rotation of the plane of polarized light) in sodium hydroxide solutions has been measured; as with most electrolytes it is nearly independent of the concentration.[232,233] Magnetic fields with gradients less than 100 oersteds per cm. cause rotation of superimposed layers of acidic and basic solutions, acids in an anti-clockwise manner and bases clockwise.[234] Magnetic fields may induce ionic motion and dipole rotation in solutions with consequent absorption of energy, and a magnetic method of following acid-base titrations, such as hydrochloric acid against sodium hydroxide, has been based on this principle.[235]

Refs. p. 690

Exchange Processes in Sodium Hydroxide Solutions

Exchange between hydrogen and deuterium in sodium hydroxide solution, where the deuterium may originate from the solvent or from the solute, has been studied. The exchange coefficients are very close to unity.[236,237]

The exchange reactions between sodium hydroxide solutions and synthetic ion-exchange resins have been studied and mechanisms have been proposed.[238,239] Sodium hydroxide is adsorbed from solution on to nylon, which is a polar fibre,[240,241] on to konjak mannan, which is colloidal,[242] and on to powdered wood, which is heterogeneous in character.[243]

Non-aqueous Solutions of Sodium Hydroxide

Solubilities of sodium hydroxide in methanol and in ethanol are given in Table XXXIII.[244]

TABLE XXXIII. - SOLUBILITY OF SODIUM HYDROXIDE IN METHANOL AND ETHANOL AT 28°C.

	g. of NaOH per 100ml. of solvent	Density of saturated solution
Methanol	23·9	1·01
Ethanol	13·6	0·93

Similar data are available for potassium hydroxide.[244] Electrical conductivities of solutions of sodium hydroxide in various alcohols have been measured, and the results have been used to calculate the mobility of the sodium ion and its effective radius in these solutions.[245] The pH of alcoholic solutions of sodium hydroxide has also been measured.[246] Infra-red absorption spectra of alcoholic solutions of sodium hydroxide show fundamental bands at 3·80μ and 5·20μ with no absorption between 5·4μ and 7μ. Energy levels are similar to those found with aqueous solutions.[247]

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CHEMICAL REACTIONS OF SODIUM HYDROXIDE

Reactions with Non-Metallic Elements

It is stated in Mellor,II,507 that alkali-metal hydroxides other than lithium hydroxide do not readily dissociate at high temperatures. This has been confirmed for sodium hydroxide; it has been observed that some decomposition occurs when the hydroxide is heated at 800°C. in hydrogen but none, even at 900°C., in nitrogen. There would appear to be some reduction by hydrogen and very little thermal dissociation.[1] When sodium hydroxide is heated in nitrogen in the presence of a number of metals and alloys, there is some decomposition at temperatures in the range 600–800°C., and sodium and sodium hydride are formed.[2]

Aqueous sodium hydroxide, like potassium hydroxide, dissolves sulphur forming a dark red solution which deposits black sulphur on standing. The solution gives the reactions of sulphides, polysulphides, thiosulphates and sulphites, and it is decomposed by carbon dioxide.[3] The ratio of thiosulphate to polysulphide increases with increasing concentration of the caustic soda solution.[4] Dilute sodium hydroxide solutions attack colloidal sulphur more rapidly than rhombic sulphur. This ability of sodium hydroxide to dissolve colloidal sulphur is applied in desulphurizing viscose rayon; sodium sulphate, sodium phosphate, borax and soap are similarly effective.[5,6] Selenium, also, is soluble in sodium hydroxide solution.[3] Fluorine forms an 'ozonate', $(KOH)_2O_2$, with potassium hydroxide in the cold, but does so less readily with sodium hydroxide solutions.[7] It is well-known that chlorination of hot, concentrated alkali solutions leads to the formation of chloride and chlorate (see Mellor,II,Suppl. I,576). Details of a process for manufacturing sodium chlorate by this reaction, and by a similar reaction with sodium bicarbonate present, have been described.[8] For the production of sodium hypochlorite bleaching solutions, sodium hydroxide is saturated with chlorine under carefully controlled conditions, which can be achieved by generating the chlorine electrolytically from a cell immersed in the sodium hydroxide solution.[9] The reaction between sodium hydroxide and chlorine can also be utilized in the analysis of chlorine-air mixtures.[10] The kinetics of the reactions between sodium hydroxide and iodine have been studied.[11,12] Low concentrations of sodium hydroxide increase the rate of formation of iodate, whilst the formation of hypoiodite (Mellor,II,Suppl. I,870) seems to be accelerated by increasing concentration of sodium hydroxide and by rise in temperature. At 50°C., with the concentration of sodium hydroxide five times that of iodine, the formation of hypoiodite is almost instantaneous. Reactions between anhydrous sodium hydroxide and carbon have been described.[13]

Reactions with Metals

The results of dissolving sodium in molten sodium hydroxide have been investigated by *X*-ray crystallography. Sodium monoxide, Na_2O, and sodium hydride, NaH, are formed,[14,15] the products acquiring a blue colour.[16] Reactions between lithium and sodium hydroxide have also been studied.[17] Magnesium imparts a blue colour to fused sodium hydroxide similar to that obtained with sodium; hydrogen is liberated, and a compound $Mg(ONa)_2$ is thought to be formed. Calcium behaves more like sodium and forms some hydride.[16]

Copper is attacked by dilute sodium hydroxide solutions at high temperatures and pressures,[18] and the mechanism of the corrosion of brass by sodium hydroxide has been described.[19] Small quantities of copper in solutions of sodium hydroxide can be measured by means of the catalytic action of copper on the reduction of ferric iron by thiosulphate.[20] The action of fused sodium hydroxide on copper has been studied; between 350° and 600°C. the amount of copper dissolved is quite small, loss in weight being only about 0·7%.[21] Its action on gold and platinum alloys has also been studied.[22] From studies on a large number of metals and alloys it has been found that only silver, nickel, zinc, copper and Monel metal show much resistance to sodium hydroxide at about 800°C.[23,24]

Sodium hydroxide solutions containing more than 0·5% of sodium hydroxide will dissolve zinc, though the extent of the dissolution does not appear to depend on the concentration of the solution. Alcoholic solutions of sodium hydroxide will not attack zinc if the solution contains less than 10% of sodium hydroxide unless an oxidizing agent such as hydrogen peroxide or oxygen itself is present, and it is concluded that the alcohol inhibits the action of the sodium hydroxide. If the concentration of alcohol exceeds 30 mol.-% there is no action at all. The solution of the zinc is best explained by two reactions:

$$\mathrm{Zn + H_2O = ZnO + H_2} \text{ followed by}$$
$$\mathrm{ZnO + NaOH = NaHZnO_2}.^{25}$$

Progress has been made in recent years with an air-depolarized primary cell containing an electrolyte of sodium hydroxide solution, a zinc or amalgamated zinc anode, and a carbon cathode. The cell reaction is probably:-

$$\mathrm{3Zn + 2NaOH + 1\tfrac{1}{2}O_2 = Na_2Zn_2O_3 + Zn(OH)_2}$$

The zinc hydroxide appears as crystals in the electrolyte of exhausted cells. The concentration of the electrolyte is 5–6·5N., and the cell then has an initial open circuit voltage of 1·45–1·47V. at 20°C. The separate standard electrode potentials are +0·13V. for the carbon cathode and -1·32V. for an amalgamated zinc anode.[26] A battery of the type zinc cathode/fused sodium hydroxide/copper oxide anode has also been described. Hydrogen liberated by the action of the electrolyte at the cathode reduces the copper oxide at the anode; the cell has an initial internal resistance of 1·949 ohms at 400°C.[27] The action of normal solutions of sodium hydroxide on cadmium-zinc alloys has been studied; if the zinc is present entirely in the eutectic it is protected by the cadmium, but if primary zinc crystals are present the cadmium accelerates the action of the sodium hydroxide.[28] The addition of aluminium to zinc lowers the rate of its solution in aqueous sodium hydroxide.[29]

Much attention has been paid to the action of sodium hydroxide solutions on aluminium and to the effect of other substances on the reaction.[30] Sodium hydroxide solutions more concentrated than 0·0004N. will attack the metal significantly even in the absence of any other reagent,[31] and pure aluminium reacts so strongly with 0·1N-sodium hydroxide solution that it cannot be passivated by anodic treatment.[32] A very active surface with a negative potential can be made by treating aluminium with boiling sodium hydroxide solution.[33] It has been suggested that the reaction proceeds through three stages:-

(1) $\mathrm{2Al + 2NaOH + 4H_2O = 2Al(OH)_2ONa + 3H_2}$
(2) the reaction is almost stationary
(3) $\mathrm{Al(OH)_2ONa + H_2O = Al(OH)_3 + NaOH}$.

The rate of the reaction increases with temperature according to the Arrhenius equation, and the concentration of sodium hydroxide also has considerable effect on the reaction velocity.[34,35] Experiments with aluminium of the highest purity (99·998% Al) have been conducted, and in spite of difficulties in obtaining reproducible results it has been found that (*a*) in concentrations below 0·5 N. the rate of dissolution is proportional to the cube root of the concentration, (*b*) in 0·5–3N. sodium hydroxide solution the rate is proportional to the concentration, (*c*) at a concentration of 3N-sodium hydroxide there is a sudden increase in the rate of solution, but at 4N. the rate is again proportional to the concentration of sodium hydroxide, (*d*) in solutions more concentrated than 5N. the solution process is very irregular, and deep pits are formed on the surface of the aluminium.[36] Techniques for obtaining reproducible results have been described.[35] The period of immersion of aluminium in sodium hydroxide solution also affects the reaction, and the rate of dissolution is inversely proportional to the immersion time.[35] A theoretical treatment of the corrosion of aluminium by solutions of sodium hydroxide has been given, which is based on studies of the action of such solutions on cylinders and spheres of aluminium.[37] When aluminium is made cathodic in sodium hydroxide solutions the rate of solution is decreased only slightly; when it is made anodic hydrogen evolution gradually stops as the current density is increased, and the loss in weight is electrochemically equivalent to the external current.[35] Chlorides, sulphates, nitrates and acetates of sodium appear to have no effect on the solution of aluminium in sodium hydroxide solutions.[31] Potassium permanganate in concentrations less than 0·06% increases the rate of dissolution, possibly because of the rapid formation of a precipitate on the aluminium surface which provides local cells. In concentrations greater than 0·1%, potassium permanganate inhibits the action of dilute sodium hydroxide solutions on aluminium.[38] Addition of sodium chromate causes passivity of the aluminium surfaces and almost completely suppresses the action of sodium hydroxide.[39,40] Sodium silicate and small quantities of silica in solution also protect aluminium against attack by sodium hydroxide, possibly by prolonging the second stage in the above scheme for the reaction.[34,41] Moreover, although a mixture of dry sodium or potassium hydroxide and powdered aluminium on contact with water releases hydrogen, which ignites in the presence of air, the addition of sufficient sodium silicate to this mixture suppresses the reaction sufficiently to prevent the spontaneous ignition of the hydrogen.[42] Protection is also afforded by agar-agar, gum arabic, gelatin, meat peptone, mannite and gum tragacanth in concentrations of about 0·4% in the sodium hydroxide solution.[35,41,43] These substances probably act by being adsorbed on the cathodic areas of the aluminium surface and so blanketing the reaction.[38] Studies of the effect on the reaction of substances in the solution should be interpreted cautiously since the presence of impurities in the aluminium itself can affect the reaction, generally increasing its rate. Iron is the most effective in this respect, having a maximum effect at a concentration corresponding to its maximum solid solubility in aluminium. The addition of magnesium, however, lowers the rate of attack by sodium hydroxide.[29] Wide grooves are formed at the grain boundaries when aluminium of high purity is corroded by sodium hydroxide solution; similar effects on aluminium containing up to 0·05% of iron indicate that these may be due to segregation of the iron in solid solution at the grain boundaries.[44] An alloy of aluminium containing 2·5% of magnesium and 0·5% of chromium (52S) dissolves in sodium hydroxide solution at a rate independent of the immersion time. Impurities such as iron accumulate on the surface of the aluminium during the reaction and cause an increase in the electrode potential. With the alloy 52S the impurities fall off the surface, and the electrode potential remains constant.[45] The potential of annealed aluminium foil can be stabilized through treatment with sodium hydroxide solutions, whilst pickling of the metal can be effected by spraying it with warm sodium hydroxide solution under slight pressure.[46,47] The corrosion of aluminium by sodium hydroxide and other solutions has also been studied in connection with the action of detergent solutions on aluminium-ware.[48]

The action of sodium hydroxide solution on zinc and aluminium can, of course, be used as methods of preparing hydrogen. Silicon, tin and lead react with sodium hydroxide in a similar manner, and a good yield of hydrogen is obtained if a 35% solution of sodium hydroxide is added ti ferrosilicon.[49] Tin dissolves in sodium hydroxide solution, sodium stannite, Na_2SnO_2, and sodium stannate, Na_2SnO_3, being formed.[50] Corrosion of tin in 1% sodium hydroxide solution is increased by small quantities of sodium chromate but sharply decreased when the concentration of this salt exceeds 2%. Tin-plate immersed in a caustic soda solution containing sufficient sodium chromate is rendered resistant to atmospheric corrosion and tarnishing by sulphur compounds.[51] The action of sodium hydroxide solution on lead has been studied under different conditions.[52-54] Results on anodic corrosion of lead in sodium hydroxide solution are confusing and do not obey Faraday's law.[55] Magnesium-lead alloys containing as much as 60% of lead are almost as resistant to corrosion by 5% sodium hydroxide solution as pure magnesium; a protective film is formed on the alloy. The intermetallic compound Mg_2Pb and alloys containing more lead are easily attacked.[56] The corrosion of titanium by sodium hydroxide solution has also been examined.[57]

The corrosion of iron by molten sodium hydroxide is an important consideration in 'caustic finishing' which is carried out at about 500°C. (see page 656). At this temperature attack on iron by molten sodium hydroxide is not extensive. At higher temperatures and in the presence of sodium peroxide reaction is more vigorous, and yellow, crystalline products with a composition corresponding to $Na_3Fe_5O_9$ are obtained. Nickel is more resistant to attack by sodium hydroxide or the sodium hydroxide-peroxide mixture but otherwise behaves similarly to iron.[21] Corrosion and mass-transfer of nickel has been found to occur more readily when a temperature gradient exists.[58] It has been observed that the presence of sodium chlorate considerably reduces the attack on cast-iron pots used in caustic finishing, and differences in the behaviour of sodium hydroxide from mercury-cathode cells, which contains no sodium chlorate, and that from diaphragm cells are due to this impurity. Less than 1% of sodium chlorate reduces the action of the sodium hydroxide by 90%.[59] The corrosion of iron by solutions of sodium hydroxide has been studied with the special object of determining which forms of iron and steel are satisfactory for use with alkaline solutions. The importance of the problem may be judged from the report that the tubes of vacuum evaporators used in the manufacture of sodium hydroxide, when made of carbon steel or of cast-iron containing much carbon, wear out in 15-90 days of use. In steam boilers, however, the sodium hydroxide present causes little attack compared with the action of other materials.[60] Steels with a high nickel content are less subject to corrosion, and steel alloys containing carbon, nickel and chromium are recommended for sodium hydroxide evaporators.[61,62] In a study of the corrosive action of the major constituents of white liquor on various steels it has been found that the action of sodium hydroxide is small compared with that of sodium thiosulphate.[63] Some of the results of experiments on the action of sodium hydroxide solutions on iron are confusing owing to the use by investigators of impure forms of the metal, such as stainless steels and graphitic cast iron. A protective film of oxide is frequently formed on the surface of the iron, and in dilute sodium hydroxide solutions, at least, this film consists of gamma ferric oxide.[64-66] It has been suggested that this film results from the action on the iron of oxygen dissolved in the solution; attack on iron by de-aerated 0·1N-sodium hydroxide solution is extremely slow.[64] With a concentrated solution of sodium hydroxide containing sodium nitrate, films of magnetite have been observed on the iron.[67] It has also been considered that the iron may at first go into solution as sodium hypoferrite, Na_2FeO_2, if the potential of the iron compared with the reversible hydrogen electrode lies between -0·7V. and -1·0V.[68] Anodic corrosion of iron in sodium hydroxide solutions leads to the formation of a solution of sodium ferrate. Under suitable conditions a concentrated solution can be obtained from which the solid ferrate can be crystallized.[69] Sodium hydroxide solutions weaker than 0·02N. have very little action on iron, and indeed sodium hydroxide in such small concentrations inhibits the corrosive action of pure water itself on iron.[70] In small amounts it can also inhibit the attack of sodium chloride solutions on iron.[71] The action of stronger solutions of sodium hydroxide on iron is inhibited by sodium sulphate, which promotes the formation of the protective oxide film on the metal. Other substances may enhance or hinder this effect of sodium sulphate.[70,72] Resistance to the action of sodium hydroxide is also acquired if the iron is previously heated to about 700°C., atmospheric oxidation presumably giving a protective oxide film.[73] Hot, concentrated solutions of sodium hydroxide may cause sub-surface corrosion of steel.[74]

A serious consequence of the attack upon iron or steel by solutions of sodium hydroxide is the subsequent failure of the metal under stress. This 'caustic embrittlement', or 'caustic cracking', is the result of the formation of intercrystalline and transcrystalline cracks following the corrosion. Dilute solutions of sodium hydroxide appear to cause little caustic embrittlement in spite of the corrosion they cause, and stress-corrosion problems are usually encountered only with hot and concentrated caustic solutions.[75-80] Silica may promote the action of sodium hydroxide especially when the latter is in dilute solution, though more recent studies have shown it to have no effect.[79,81,82] Steel and cast-iron may be satisfactorily hardened by being quenched in sodium hydroxide solutions; a more uniform surface hardness results than by quenching in water.[83-85] An extremely effective method of protecting steel from the action of sodium hydroxide solutions consists in coating the metal with polystyrene or a cellulose ether.[86,87] Hot solutions containing more than 70% of sodium hydroxide can be transported in tank-cars lined internally with polystyrene.[87]

Comparisons have been made of the rate of corrosion of a number of metals and alloys by sodium hydroxide and other solutions.[88] Nickel and nickel-rich alloys are more resistant than iron.[89] Nickel is not attacked by caustic solutions if it is made the cathode carrying a very low current density; nickel-lined tank-cars in which the nickel is made the cathode and the anode is of some material not affected by sodium hydroxide are used for transporting caustic solutions.[90]

Reactions with Acids

The neutralization of sodium hydroxide solutions by acids has been studied electrometrically in systems with a polarized platinum electrode and in a number of bimetallic electrode systems.[91,92] In titrations between dilute orthophosphoric acid and sodium hydroxide only two inflexions have been observed in the titration curve, and these correspond to the formation of NaH_2PO_4 and Na_2HPO_4.[91,93-95] Titrations between sodium hydroxide and orthoboric acid have been studied by a thermometric method, and the formation of NaH_2BO_3 demonstrated.[96] Neutralization of hydrochloric acid with sodium hydroxide has been studied by measurement of viscosity, density, refractive index, conductivity and magnetic susceptibility of the solutions, and by the use of phenol as a second liquid phase.[97,98] It has been found that temperature has no effect on the neutralization of sodium hydroxide by mono-, di- and tri-basic acids.[99] The heat of neutralization has been evaluated and found to be 13·7 kg.-cal., though slightly lower values have also been reported.[100-102] The value of the heat of reaction between hydrochloric acid and sodium hydroxide has been used in a study of the rate of interdiffusion of two reacting liquids under conditions where mechanical mixing is avoided.[103] A contraction in volume occurs when solutions of sodium hydroxide or other bases are neutralized, the maximum contraction occurring at the point of neutral salt formation. The effect is attributed to changes in the hydration of ions in the solution.[104,105]

Radiations in the ultra-violet or near ultra-violet have been observed in the neutralization of sodium hydroxide by the mineral acids; the radiation is more intense with 1N. than with 5N. solutions. It has been suggested that the effect is due to the excitation of ions to a higher energy level by means of the energy liberated by the neutralization reaction.[106-110]

The neutralization of sodium hydroxide and hydrochloric acid in non-aqueous solvents such as methanol and ethanol has also been studied.[111]

Systems of Sodium Hydroxide and Alkali and Alkaline-earth Salts

Solubility relationships in the system $NaOH$-Na_2CO_3-H_2O have been thoroughly examined; the following hydrates of sodium hydroxide have been observed in this system at 0°C.: $NaOH$, $NaOH,H_2O$, $NaOH,2H_2O$, $NaOH,3{\cdot}5H_2O$ and $NaOH,4H_2O$.[112-113] Anhydrous sodium hydroxide reacts with sodium cyanide above 500°C., forming sodium carbonate, sodium cyanamide, sodium monoxide and hydrogen. In the presence of a little water the reaction occurs more readily and at a lower temperature and is accompanied by hydrolysis reactions.[114]

Thermal analysis of the system $NaOH$-$NaNO_3$ indicates the formation of two compounds, $2NaOH,NaNO_3$ and $NaOH,NaNO_3$, but neither of these has yet been crystallized from aqueous solution. They can be formulated as salts of the hypothetical orthonitric acid, Na_3NO_4,H_2O and Na_2HNO_4. The double salt $NaOH,NaNO_2$ has been observed in melts of sodium hydroxide and sodium nitrite.[115-117] When sodium hydroxide is heated with an alkali-metal nitrate in the presence of various non-metals evolution of ammonia occurs.[118]

The tetrahydrate, $NaOH,4H_2O$ can exist at low temperatures in the system $NaOH$-Na_2SO_3-H_2O, but at higher temperatures only the monohydrate is observed.[119] This is the only one that can exist at any temperature in the system $NaOH$-$NaCl$-H_2O.[112,120,121] Thermal analysis of the anhydrous system $NaOH$-$NaCl$ from 150° to 800°C. shows that mixed crystals but no compounds are formed.[120,121]

The double salt $NaOH,HCO_2Na$ is formed from molten mixtures of sodium hydroxide and sodium formate.[122] Various hydrates and eutectics can be crystallized from mixed aqueous solutions of the hydroxide and sodium acetate, but no double salt has been observed.[123] The double salts $NaOH,$-$Na_2C_4H_4O_6,3H_2O$ and $4NaOH,3Na_2C_4H_4O_6$ have been obtained as crystals from mixed solutions of sodium hydroxide and sodium tartrate.[124] A double salt of sodium hydroxide and Rochelle salt has also been reported, but its composition is unknown.[125] The addition of sodium hydroxide to solutions of uranyl tartrate causes an increase in their rotatory power, which becomes a maximum when 1 mole of sodium hydroxide per mole of tartaric acid has been added; an addition compound or complex is probably formed.[126]

Systems involving sodium hydroxide, calcium sulphate and calcium carbonate have been studied to obtain data on the solubility of calcium carbonate in sodium carbonate and sodium hydroxide and to deduce causes of the formation of scale in boilers.[127]

Reactions with Metal Salts

When sodium hydroxide solution is added to solutions of cupric sulphate precipitates of cupric hydroxide are obtained, the characteristics of which depend on the amount of alkali used. The hydration of the precipitate decreases with increasing quantity of sodium hydroxide, and if an excess of sodium hydroxide is used a precipitate can be obtained which is insoluble in ammonium hydroxide. Complete precipitation of all the copper from a solution of copper sulphate can be achieved by the addition of less than the calculated amount of sodium hydroxide. This has been explained by the adsorption of sulphate on the precipitate of cupric hydroxide, an effect which decreases with further addition of sodium hydroxide.[128,129] Precipitates of basic copper sulphates have been observed when the addition of dilute sodium hydroxide to dilute cupric sulphate solution has been followed thermometrically and potentiometrically. The compounds $CuSO_4,3CuO$ and $CuSO_4,CuO$ have been reported, and the results appear to suggest that cupric hydroxide is not formed directly.[130-132] Pseudomorphs of cupric hydroxide have been observed, however, when 2N-sodium hydroxide solution is added to crystals of various copper salts.[133] A basic copper phenoxide has been reported to be formed when solutions of phenol, a copper salt, and sodium hydroxide are mixed.[134] The reaction between sodium hydroxide and chloroauric acid has also been investigated, and the results indicate the formation of sodium aurate, $NaAuO_2$, in solution.[135]

The heat of reaction between beryllium sulphate and sodium hydroxide, both in solution, has been measured and is 17·5 kg.-cal.[136] Magnesium hydroxide is precipitated when sodium hydroxide and magnesium salt solutions are mixed; the basic nitrates $Mg(NO_3)_2,Mg(OH)_2$ and $Mg(NO_3)_2,4Mg(OH)_2$ are also formed when sodium hydroxide is added to magnesium nitrate solution.[137,138]

There is disagreement as to whether basic zinc salts are precipitated when sodium hydroxide is added to solutions of zinc nitrate or zinc sulphate.[132,138-141] However, complete removal of zinc from a solution can be effected with less than the calculated amount of sodium hydroxide, and it has been suggested that, as with cupric hydroxide, anions are adsorbed on precipitates of zinc hydroxide, the adsorption diminishing with further addition of alkali.[142] Basic salts of cadmium are precipitated by sodium hydroxide from solutions of cadmium nitrate or cadmium sulphate.[138,143,144]

When sodium hydroxide solution is added to solutions of aluminium salts the precipitate formed may consist of basic salts, hydrous aluminium oxides, or the various forms of sodium aluminate. Precipitation of the aluminium is completed before all the sodium hydroxide required to produce $Al(OH)_3$ is added. This may be due to the formation of a basic salt of aluminium or to adsorption of solute materials by the initial precipitate. For example, it has been found that when 2–4 moles of sodium hydroxide are added to 1 mole of potassium aluminium sulphate the composition of the precipitate remains constant and analysis shows it to be a basic aluminium sulphate.[145] The precipitation process is undoubtedly a complex one and depends on the nature of the aluminium compound, the concentration of the reagents, the temperature and the rate of mixing of the solutions.[146-148] The precipitation of gallium and indium hydroxides is also completed with less than the stoicheiometric proportion of sodium hydroxide. Virtually pure gallium hydroxide, $Ga(OH)_3$, is precipitated quantitatively from gallium chloride solutions with only 2·8–2·9 equivalents of sodium hydroxide; basic sulphates are precipitated from gallium and indium sulphate solutions.[149,150] Hydroxides precipitated from gallium or indium chloride solutions by sodium hydroxide do not adsorb solute material as does aluminium hydroxide.[148]

From solutions of lead salts sodium hydroxide precipitates basic salts. Changes in the pH of dilute lead chloride solutions when titrated with sodium hydroxide solution have been explained by the formation of $PbO,PbCl_2$ and $3PbO,PbCl_2$; these, with PbOHCl and similar basic bromides, are reported to have been isolated.[151-154] Several basic nitrates may be formed by the addition of sodium hydroxide to lead nitrate solutions; the most basic is possibly $Pb(NO_3)_2,9Pb(OH)_2$. Lead hydroxide is said to be difficult to prepare, possibly because of the re-dissolution of the basic salt precipitates to form soluble plumbites.[138,155]

Sodium hydroxide causes precipitation of chromic hydroxide from solutions of chromic salts. However, addition of 2–5 moles of sodium hydroxide to 1 mole of potassium chromium sulphate gives a basic chromium sulphate of constant composition.[156] Mixed hydroxides are precipitated from solutions containing zinc and chromium or nickel and chromium salts.[132] The action of sodium hydroxide on solutions of ammonium molybdate is two-fold; at first the polyanion of the ammonium salt is broken down to the normal MoO_4'' ion, and then the ammonium ion is displaced by the sodium.[157] Addition of sodium hydroxide to solutions of uranyl chloride causes precipitation of $U(OH)_6$; from uranyl nitrate solutions, however, basic salts are formed, and there is also evidence of the formation of uranates.[158,159]

Precipitation of hydrated ferric oxide from ferric chloride solutions can be achieved with less than the calculated quantity of sodium hydroxide. This is probably due to the adsorption of chloride by the initial precipitate, the adsorption being reduced on further addition of sodium hydroxide. Addition of excess of sodium hydroxide at high temperatures results in a precipitate resistant to acids.[160] The volume changes observed when ferric chloride and sodium hydroxide solutions are mixed are not in accord with a simple dilution of sodium chloride, the only soluble product of the reaction.[161] Basic sulphates are produced by addition of sodium hydroxide to ferric sulphate solution, the ratio Fe_2O_3/SO_3 being dependent on the pH of the solution and rising with pH. Excess of sodium hydroxide must be added to obtain a sulphate-free precipitate.[162-164] Other results from pH titrations on ferric sulphate, chloride, or nitrate solutions, however, indicate that no basic salts are formed.[132] Nickel hydroxide only, and no basic salts, is precipitated by sodium hydroxide from nickel solutions.[132] A complex nickel borate is formed when sodium hydroxide is added to nickel sulphate solutions containing boric acid.[165]

Reactions with Metal Oxides and Hydroxides

Copper hydroxide is soluble in sodium hydroxide solution especially if this is concentrated, though above a certain concentration of sodium hydroxide the solubility of copper hydroxide diminishes. Blue, and in one case violet, solutions are obtained which decompose on standing, yielding precipitates that are said to be solid solutions of cupric oxide and cupric hydroxide. The maximum solubility of copper hydroxide in sodium hydroxide solutions corresponds to the formation of a cuprate, probably Na_2CuO_2. Solid cuprates have been prepared from these blue solutions, though their composition is uncertain. Copper oxide is also soluble in sodium hydroxide solutions though less so than the hydroxide.[133,166-169] Solubility of the hydroxide in sodium hydroxide solutions is said to be 'induced' by the presence of chromic hydroxide.[170] It has been assumed that the cuprate solutions contain the anion $Cu(OH)_4''$, and an equilibrium constant has been evaluated from thermal data for the reaction:-

$$Cu^{++} + 4OH^- = Cu(OH)_4^{--}.$$[171]

Sodium hydroxide has no solvent action on calcium or barium hydroxide; the solubility of these decreases in the presence of sodium hydroxide, that of calcium hydroxide reaching a minimum in 0·35N-sodium hydroxide.[172-174] The solubility of magnesium hydroxide can be induced by the presence of sufficient chromic hydroxide.[170] Zinc hydroxide is soluble in sodium hydroxide solution. Small quantities of the alkali produce a colloidal solution of zinc hydroxide, but with larger quantities a solution containing zincate ions results.[175,176] The solubility of zinc hydroxide in solutions of sodium hydroxide decreases with rise in temperature.[177] The composition of sodium zincate and of the zincate ion have been studied by the application of electrometric and thermal analysis methods, and there appear to be two forms of the compound, which occur at different concentrations of sodium hydroxide. A monosodium salt $Na[Zn(OH)_3]$ can be obtained from 13·5–19·6N-sodium hydroxide solutions, and a disodium salt, $Na_2[Zn(OH)_4]$, from more concentrated solutions.[178,179] The salts $NaHZnO_2$, $NaHZnO_2,4H_2O$ and Na_2ZnO_2 have also been reported and methods described for their preparation.[180,181] The equivalent conductivity of solutions of sodium hydroxide is lowered steadily by addition of zinc hydroxide, and it has been inferred that at a given sodium hydroxide concentration only one species of zincate ion occurs in solution.[175,182] The examination of fused mixtures of sodium hydroxide and zinc oxide has been described.[183,184] Cadmium hydroxide can be brought into solution in sodium hydroxide in the presence of sufficient chromic hydroxide.[170] Mercuric oxide is soluble in solutions of sodium hydroxide, and there is a steady increase in the solubility as the concentration of sodium hydroxide increases. It has been inferred that mercuric oxide behaves as a weak acid, and values of the dissociation constant of a mercuric acid have been deduced.[185]

It is well-known that aluminium hydroxide is soluble in solutions of sodium hydroxide. The solubility appears to be a maximum in 10N-sodium hydroxide solution.[186,187] The rate at which aluminium hydroxide dissolves is low even in hot sodium hydroxide solutions.[188] The aluminate $NaAlO_2$ is reported to be formed.[189] Aluminium hydroxide may be reprecipitated from its solution in sodium hydroxide in various ways, for example, by adding carbon dioxide to the solution.[190] The behaviour of aluminium oxides towards sodium hydroxide solution is important in connection with the action of such solutions on aluminous minerals. Bauxite can be dissolved in sodium hydroxide solution sufficiently concentrated that it may be heated to 160–165° C. without increase in pressure;[191] in dilute sodium hydroxide solutions only gibbsite dissolves.[192] When aluminium silicates such as dickite or kaolinite are treated with a 10% solution of sodium hydroxide the aluminium and silicon in the mineral dissolve to the same extent. When these minerals are heated with sodium hydroxide solution under pressure the insoluble $Na_2Al_2SiO_6,2H_2O$ is formed.[193] The aluminate $NaAlO_2$ has been identified by X-ray methods in the product of heating sodium hydroxide and aluminium oxide to 950° C.[194] Others have reported the aluminate as $Na_2Al_2O_4$.[195] If a mixture of sodium hydroxide, aluminium oxide, and iron is heated in air, the products include sodium ferrite, $NaFeO_2$, and sodium ferrate, Na_2FeO_4.[194] Thallic hydroxide can be brought into solution in sodium hydroxide if sufficient chromic hydroxide is present.[170] Ceric oxide and sodium hydroxide are reported to form Na_2CeO_3.[195]

The action of sodium hydroxide solutions on silicon dioxide is to a large extent determined by the physical form of the silica. Silica gel adsorbs sodium ions from dilute sodium hydroxide solutions; more concentrated solutions dissolve the gel.[196,197] Quartz, also, will adsorb sodium from sodium hydroxide solutions.[198,199] When quartz or fused silica is heated with sodium hydroxide solution under pressure, silicates with a high silica content are formed, and these remain in solution or are deposited according to the concentration of the solution. Weak sodium hydroxide solutions cause conversion of fused silica into a form of cristobalite.[200,201] The reaction between sand and fused sodium hydroxide has also been studied; the reaction does not seem to go to completion.[202] Silicates are attacked by solutions of sodium hydroxide. Sodalite, $Na_8Al_6Si_6O_{24}(OH)_2,aq.$, is formed from the calculated proportions of sodium hydroxide and kaolin; other products result from different proportions of these reactants.[203,204] Etch figures in the form of isosceles triangles are made on samples of muscovite by fused sodium hydroxide at 350° C.; the etching proceeds faster if the sodium hydroxide has been dehydrated previously at a higher temperature.[205] The equilibria between solid sodium silicates and fused sodium hydroxide has been studied by measurements of the water vapour pressure at equilibrium and by X-ray examination of the products.[206] The behaviour of stannic acid sols towards sodium hydroxide has been studied; the sol is only partially soluble even in an excess of sodium hydroxide.[207,208] Lead hydroxide is soluble in sodium hydroxide solution, though the solubility decreases at high alkali concentrations owing to transformations in the solid phase.[209] Sodium titanates are formed when sodium hydroxide and titanium oxide are heated together, and three different products have been identified.[195] If zirconium oxide is heated with sodium hydroxide a zirconate is formed which is reported to be Na_2ZrO_3.[195] When sodium hydroxide is heated with zircon at 600° C. the products are soluble sodium silicate and an insoluble sodium zirconate.[210]

The adsorption curve for sodium hydroxide on arsenious oxide shows two breaks corresponding to the formation of NaH_2AsO_3 and Na_2HAsO_3.[211] Calcined niobium pentoxide reacts with solutions of sodium hydroxide forming a salt reputed to be $Na_{14}Nb_{12}O_{37},32H_2O$; other sodium niobates yield this same salt when they are fused with sodium hydroxide and the melt is treated with water.[212-214]. In conductometric titrations of sodium hydroxide with telluric acid, H_6TeO_6, the following salts have been detected: NaH_5TeO_6, $Na_2H_4TeO_6$, $Na_4H_2TeO_6$ and Na_6TeO_6. The last two were not detected in pH and thermometric titrations. The disodium salt is easily isolated by mixing solutions of telluric acid and excess of sodium hydroxide; it loses water at 170° C. to form Na_2TeO_4.[215]

Chromium oxide and chromium hydroxide are soluble in solutions of sodium hydroxide yielding the chromite, $Na_2Cr_2O_4$.[195] With precipitated chromium hydroxide the extent and the readiness of the dissolution depends on the age of the precipitate.[216,217] With solutions of the correct strength a sol of chromium hydroxide in sodium hydroxide can be formed; it is not, however, stable.[218] A stable chromic hydroxide sol can be obtained if excess of sodium hydroxide is added to a chromium solution containing a suitable non-electrolyte as a peptizing agent.[219] Chromium trioxide, CrO_3, dissolves in sodium hydroxide solution with the formation of sodium chromate, and sodium hydroxide will convert potassium dichromate into the sodium salt.[195,220] Insoluble tungstic acids are peptized by low concentrations of sodium hydroxide.[221]

Manganese hydroxide can be brought into solution with sodium hydroxide if sufficient chromic hydroxide is present as well.[170] Manganese hydroxide in boiling concentrated sodium hydroxide solution is oxidized by oxygen, the light-brown sodium salt $NaMnO_2$ being formed; other manganites can be obtained at lower temperatures.[222] Manganese dioxide mixed with sodium hydroxide is oxidized by air to sodium manganate; this is easily hydrolyzed by steam with re-formation of the reactants, and the two-fold reaction has been proposed as a means of producing very pure oxygen.[223]

Freshly precipitated hydrated ferric oxide adsorbs acids, especially from dilute solution, whilst its adsorption of sodium hydroxide is small.[224] These precipitates can be peptized by alkaline solutions of mannitol and sodium tartrate.[225,226] Peptization can also be effected if the ferric hydroxide is mixed with sufficient chromic hydroxide.[170,227] Reaction between anhydrous sodium hydroxide and ferric oxide leads to the formation of sodium ferrite, $Na_2Fe_2O_4$, and sodium ferrate, Na_2FeO_4.[195] Ferrous hydroxide, which is so easily oxidized by air, is less readily oxidized when kept in alkaline solution. This has been attributed to the lower solubility of oxygen in solutions of sodium hydroxide.[228]

Reactions with Miscellaneous Inorganic Substances

Sodium hydroxide has been observed to accelerate the decomposition of hydrogen peroxide, the effect being dependent on the concentration of sodium hydroxide.[229,230] Sodium hydroxide also increases the rate of the reaction between hydrogen peroxide and potassium permanganate.[231]

Solid sodium hydroxide absorbs hydrogen cyanide readily.[232] Carbon monoxide dissolves very slightly in solutions of sodium hydroxide, sodium formate being formed.[233-235] The extent of the absorption is, however, so small that the amount of carbon monoxide in mixtures with carbon dioxide and certain other gases can be found by dissolving all except the carbon monoxide in sodium hydroxide solution.[236] Nevertheless, it has been calculated from thermodynamic data that the reaction $NaOH + CO \rightleftharpoons HCO_2Na$ should go to completion even with very low partial pressures of carbon monoxide, though the rate, of course, is extremely small.[237] The reaction is autocatalytic, and this is attributed to the greater rate of absorption of carbon monoxide by sodium hydroxide when sodium formate is present.[238] The reaction between carbon dioxide and solutions of sodium hydroxide has been studied under a variety of conditions. When the gas is passed over, or allowed to remain in contact with, a large bulk of unstirred solution the velocity of the reaction is controlled by a number of factors, among them being the pressure of the gas and the concentration of the solution.[233,236,239-243] The rate-determining factor may be the low rate of diffusion of carbon dioxide through the solution; alternatively it has been suggested that the velocity of the reaction is determined by the rate of diffusion of sodium hydroxide through the solution to the gas-liquid interface where the reaction takes place.[244,245] The reaction between carbon dioxide and a stirred solution of sodium hydroxide is partly dependent on the viscosity of the solution. The viscosity of sodium hydroxide solutions has been altered by the addition of sugars and other substances, and while considerable changes in the rate of absorption of carbon dioxide have resulted little correlation between these changes and the viscosity has been found. Absorption of carbon dioxide by sodium hydroxide in agar-agar jelly has also been studied.[246-249] The absorption of carbon dioxide is more rapid when the gas is bubbled through sodium hydroxide solution. The size of the bubbles and their depth in a solution affect the absorption, which is slower in sodium hydroxide solution than in potassium hydroxide.[243,245,250-253] Other conditions under which absorption has been studied include passing the gas through the solution in columns packed with glass rings,[254,255] and passing drops of the solution through an atmosphere of the gas.[245] Forms of solid sodium hydroxide recommended for absorption of carbon dioxide in analytical work include soda-lime, 'pulverized household lye',[256,257] granules 0·2–0·25 in. in diameter,[258] and as a deposit on asbestos (Ascarite).[259] The heat of combination of sodium hydroxide with 1 g.-mol. of carbon dioxide has been found to be 10,690 g.-cal.[260] The reaction between sodium hydroxide solution and carbon disulphide takes place in a number of steps. It seems to be agreed that the final result can be represented by the equation:-

$$6NaOH + 3CS_2 \rightarrow Na_2CO_3 + 2Na_2CS_3 + 3H_2O,$$

but there are different views on the several stages of the reaction. Some authors have reported the initial formation of sodium sulphide, Na_2S, which combines with further carbon disulphide forming sodium thiocarbonate.[261-263] Others state that sodium sulphide is not formed but that the compound Na_2CS_2O is produced instead and that this functions as an intermediate in the following way:-

$$CS_2 + 2NaOH \rightarrow Na_2CS_2O + H_2O$$
$$3Na_2CS_2O \rightarrow 2Na_2CS_3 + Na_2CO_3.$$[264,265]

Whatever the mechanism may be, the reaction is slow and takes several days for completion.[236] When sodium hydroxide absorbs carbon disulphide from solutions of the latter in benzene, the reaction is believed to be controlled by the diffusion of carbon disulphide across the liquid-liquid interface.[266] Carbonyl sulphide is absorbed fairly rapidly by sodium hydroxide solution.[236]

Siloxanes react with sodium hydroxide solution, and a comparison has been made between the ease with which sodium hydroxide attacks Si–Si, Si–H and Si–O–Si bonds.[267] Sodium hydroxide reacts with natural samples of galena forming compounds which prevent the flotation of the galena with xanthate; potassium hydroxide hinders the flotation process still more.[268]

The solubility of ammonia in sodium hydroxide solutions has been studied. At atmospheric pressure a 60% solution of sodium hydroxide dissolves no ammonia; the solubility of the gas then rises with decreasing concentration of sodium hydroxide.[269] The system $NaOH-NH_3-H_2O$ has also been studied at higher pressures where liquid phases co-exist, one rich in ammonia. Liquid ammonia, anhydrous or containing very little water, will dehydrate sodium hydroxide solutions; certain impurities in these solutions are extracted into the ammonia phase, and substantially pure sodium hydroxide is thereby obtained.[270-278] (See page 659).

There is a slow reaction at ordinary temperatures between sodium hydroxide and nitric oxide with the formation of sodium nitrite, nitrous oxide, and nitrogen. Other alkali and alkaline-earth hydroxides behave in a similar way.[279] Sodium hydroxide solution will extract most of the phosphorus from soils except where the phosphate is present as an apatite.[280] A reaction has been reported between bismuth sulphide and sodium hydroxide in which metallic bismuth is formed.[281]

The heat of neutralization of hydrogen sulphide with sodium hydroxide has been measured and is 8·44 kg.-cal.; for the half-neutralization and formation of NaHS it is 8·18 kg.-cal.[282] The absorption of hydrogen sulphide by solutions of sodium hydroxide has been considered theoretically.[283] The heat of neutralization of sodium hydroxide with sulphurous acid has been found to be 31·49 kg.-cal.[284] This value may be contrasted with that of 13·7 kg.-cal. obtained for the neutralization of sodium hydroxide with the mineral acids.[100-102]

Sodium hydroxide solutions react easily with fluorine monoxide, the reaction presumably being:-

$$F_2O + 2OH^- \rightarrow O_2 + 2F^- + H_2O.$$[285]

With methoxyfluoboric acid and with monohydroxyfluoboric acid sodium hydroxide forms sodium fluoborate.[286] The heat of neutralization of hypochlorous acid with sodium hydroxide (and with other hydroxides) has been found to be 8940 g.-cal.[287] Chlorites can be formed from sodium hydroxide and other basic solutions by adding chlorine dioxide and hydrogen peroxide.[288] The kinetics of the reaction between sodium hydroxide and chlorine dioxide have been studied.[289] In the system $NaIO_4-NaOH-H_2O$, three stable sodium salts have been obtained: $NaIO_4,3H_2O$, $Na_2H_3IO_6$ and $Na_3H_2IO_6$.[290]

Reactions with Organic Substances

The reactions of sodium hydroxide with organic substances are in general outside the scope of this Treatise. The following paragraphs deal only with those reactions which might be of interest to inorganic chemists.

A number of simple organic compounds react with fused sodium hydroxide in the temperature range 250–450° C. with the formation of hydrogen, methane and sodium carbonate, or in some cases sodium orthocarbonate. Acetylene reacts according to the equation:-

$$C_2H_2 + 4NaOH \rightarrow Na_4CO_4 + H_2 + CH_4.$$

Refs. p. 709

With ethyl alcohol the reaction may involve two stages:-

$$C_2H_5OH + NaOH \rightarrow CH_3COONa + 2H_2 \text{ and}$$
$$CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3.$$

Other monohydric alcohols and some esters behave similarly, except methyl alcohol which does not yield methane. Acetaldehyde reacts with fused sodium hydroxide at 250°C. forming sodium carbonate and hydrogen, while at 300°C. it yields methane as well. Formaldehyde, however, does not yield methane at any temperature. Glycol is oxidized by fused sodium hydroxide at 350°C. to sodium carbonate and hydrogen; glycerol yields methane as well under the same conditions. Dextrose, lævulose and cellulose all yield carbonates, hydrogen and methane with fused sodium hydroxide, but sucrose undergoes extensive carbonization. Methylamines, dimethyl ether and diethyl ether do not react with fused sodium hydroxide.[291-295]

With aqueous sodium hydroxide, formaldehyde forms sodium formate and methyl alcohol. The reaction is believed to occur in two stages:-

$$HCHO + NaOH \rightarrow HCOONa + H_2 \text{ and}$$
$$HCHO + H_2 \rightarrow CH_3OH,$$

the first being promoted by cuprous or silver oxide.[296] A more complex series of reactions has been reported with 40% formaldehyde and sodium hydroxide solution of density 1·5 g. per c.c., sugars, aldehydes and formates being produced.[297,298] White, hygroscopic crystals of $3NaOH,2H_2O,CH_3OH$ are formed when methyl alcohol and aqueous sodium hydroxide solution are mixed at 70°C. and then cooled. The compound may be used in the purification of sodium hydroxide.[299] A similar compound, $3NaOH,xH_2O,C_2H_5OH$, where x is probably 3, can be crystallized from aqueous-alcoholic solutions of sodium hydroxide at 17°C.[300] Electrolysis of alcoholic solutions of sodium hydroxide has been studied; the chief product is acetaldehyde and secondary products include aldehyde resins, aldol, crotonaldehyde and other compounds of high molecular weight.[301] The formation of polyvinyl alcohol from polyvinyl acetate and sodium hydroxide in absolute methyl alcohol has been investigated. Sodium hydroxide forms an addition compound with polyvinyl alcohol, the amount of sodium hydroxide held in combination varying with the concentration of the reacting solutions. The infra-red spectrum of the compound has been reported.[302-304]

A grey, metallic hygroscopic powder with a sulphurous smell is obtained when acetone, sulphur and sodium hydroxide are heated under reflux. It can be used for agricultural purposes in place of sulphur.[305] $\alpha\beta$-Unsaturated aldehydes suffer cleavage at the double bond when heated with 25–50% sodium hydroxide solution at 200°C.[306] The reactions between sodium hydroxide and alkyl chlorides or hydroxy-halogeno compounds have also been studied.[307-309] The isotopic dilution method of analysis has been used in the study of the decomposition of certain hexose sugars in dilute sodium hydroxide solution.[310] Polymeric anhydro-sugars form addition compounds with sodium hydroxide of the type $(C_{12}H_{20}O_{10},NaOH)_x$; an inulin compound, $(C_6H_{10}O_5,NaOH)_x$, has been prepared by dissolving inulin in 8% sodium hydroxide solution and crystallizing from absolute alcohol.[311,312] The decomposition of starch by sodium hydroxide solution proceeds very slowly, and addition compounds are formed simultaneously. These correspond to similar cellulose compounds, though unlike the cellulose compounds the starch compounds show sharp transitions from one to another, which indicates an absence of topochemical fixation.[313,314]

Salts of sodium hydroxide and certain cyclic imides and anils are formed when these are shaken together in various solvents. Succinimide, for example, forms the compound $C_4H_4O_2NH,2NaOH$. Similar potassium salts are also formed. It has been suggested that the metal is held in O–Na rather than N–Na combination.[315] The action of sodium hydroxide on sodium picrate has been investigated spectrophotometrically. There are two reactions, and in one, which is favoured by light, ammonia is formed.[316] A red compound is formed between barbituric acid, picric acid and sodium hydroxide when ethyl alcohol is added to a suitable mixture of these three.[317] Reactions of sodium hydroxide with pyrazole and some of its derivatives have been studied.[318]

Sodium hydroxide promotes the condensation of formaldehyde and phenol, though other bases are also effective.[319,320] Sodium hydroxide also aids in the oxidation of alkali lignin; it has been suggested that the lignin exists in keto and enol forms, the more easily oxidized enol form being favoured by the alkali.[321,322] The combination of sodium hydroxide and gelatin has been investigated; in approximately decinormal solutions of sodium hydroxide the gelatin molecule appears to undergo a change in structure.[323,324] The action of sodium hydroxide on wool keratin and on some synthetic polymers has also been studied.[325-327]

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ANALYTICAL CHEMISTRY OF SODIUM HYDROXIDE

Preparation of Standard Solutions of Sodium Hydroxide

Sodium hydroxide is an important reagent in volumetric analysis, but its usefulness can be affected by the readiness with which it absorbs carbon dioxide and reacts with glass storage vessels. Standard solutions have been made by passing sodium chloride solutions through anion exchange resins; the eluent, sodium hydroxide solution, is collected in a volumetric flask and suitably diluted. The usual precautions are necessary to prevent access of carbon dioxide.[1] The effect of storing standard solutions for long periods of time in vessels of Jena glass has been studied.[2] It may be preferable to store a concentrated solution and to dilute a filtered portion of this whenever a standard caustic solution is required.[3] A dilute solution of sodium hydroxide may be kept for some time in a nickel vessel without undergoing any change in concentration,[4,5] and polystyrene bottles may also be suitable.[6] A number of suggestions have been made for preparing and storing sodium hydroxide solutions for teaching purposes.[7,8] Tables have been published showing the variations of the concentration of sodium hydroxide solutions with changes in temperature, and some values are shown in Table XXXIV.

TABLE XXXIV. - VARIATION OF NORMALITY OF SOLUTIONS OF SODIUM HYDROXIDE WITH TEMPERATURE

Temperature at which solution is Normal	Normality at 5°C.	Normality at 30°C.
15°C.	1·00245	0·99508
20°C.	1·00393	0·99655
25°C.	1·00559	0·99819

Determination of Sodium Hydroxide

The determination of sodium hydroxide is frequently complicated by the presence of sodium carbonate. The methods of determining sodium hydroxide in the presence of sodium carbonate are fully described in the standard text-books on chemical analysis. Briefly, they include the precipitation of the carbonate as barium carbonate; the use of two indicators, phenolphthalein and methyl orange; or a pH method based on the knowledge of the pH changes taking place when neutralization reactions are complete.[10-19] Sodium hydroxide solutions can be titrated with luminol as an indicator and the end-point detected photometrically.[20] The end-point with sodium hydroxide solutions can also be detected with a high-frequency oscillator.[21,22] The titration of very small volumes of solutions presents difficulties which have been investigated using solutions of sodium hydroxide.[23,24] The spectrochemical analysis of sodium hydroxide has been described.[25,26] The separation of sodium hydroxide from other alkali metal hydroxides can be done chromatographically, on columns and on paper.[27]

Caustic soda solutions used in the wood-pulping, artificial textile, and other industries do not need to be analyzed completely for the purpose of following and controlling their composition. Thus the total alkali content may be estimated from pH measurements of the solutions. Analysis may be complicated by the presence of sodium sulphide, but this can be removed with oxidizing agents. Other difficulties may be caused by the colour or fluorescence of the solutions.[28-36] Small traces of alkali in textile fibres can be detected with a dilute solution of methyl green, which is decolourized when boiled with alkali.[37]

The Determination of Metallic Impurities in Sodium Hydroxide

Magnesium in sodium hydroxide can be determined by a photometric method with Thiazole Yellow, after other metals have been removed.[38] For the determination of zinc a complex potassium zinc iodide is formed prior to the titration of the alkali with hydrochloric acid.[39] Very small amounts of iron can be determined by an electrolytic method.[40] Manganese can be determined by a method which involves oxidation to permanganate with ammonium persulphate in the presence of silver nitrate.[41] Traces of copper in sodium hydroxide can be determined photometrically with sodium diethylthiocarbamate; to prevent interference by nickel the latter is complexed as the ethylenediaminetetraacetate.[42]

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APPLICATIONS

Some idea of the scale of the present-day production of sodium hydroxide may be obtained from the following figures for output in the United States of America:-

1940	1,100,000 short tons
1945	1,800,000
1949	1,918,000.

The uses to which this one substance is put are widespread. They include,[1-4] the manufacture of rayon (400,000 short tons in 1945) and of other chemicals; the refining of petroleum products; the manufacture of wood-pulp, paper and soap; the treatment of textiles, rubber and vegetable oils and the manufacture of cleaning materials other than soap.

The Manufacture of Wood-pulp

Wood-pulp, required for paper-making, is obtained mainly by three methods. Wood with a low resin-content is digested with calcium bisulphite solution, while resinous woods, chiefly coniferous, are digested with sodium hydroxide solution according to the Kraft process. Coniferous woods may also be treated with sodium sulphate solution to which a small amount of sodium hydroxide is added.

In the Kraft process sodium hydroxide solution of 5–14% concentration is used at temperatures from 10° to 50° C. Hemicelluloses and some of the lignin are dissolved from the wood, and the lattice structure of the remaining celluloses probably undergoes some change. Prolonged treatment, or the use of more concentrated sodium hydroxide, renders the pulp unsuitable for paper-making.[5-15] The strength and flexibility of the wood-pulp are improved considerably if it is treated with chlorine after the digestion with sodium hydroxide.[16,17] Much of the development in the industry in recent years has been in the recovery processes used to extract the sodium hydroxide from the so-called green liquor after this has been drained from the pulp. In the process of digestion sodium carbonate is formed, and this is reconverted to sodium hydroxide by electrolytic methods or by the lime-soda process. Recoveries of 99% are claimed.[18-28]

If wood shavings are digested with a mixture of sodium sulphate and sodium hydroxide a smaller proportion of the lignin is extracted than in the Kraft process, and the pulp obtained is suitable for the manufacture of very strong papers. Moreover the pulp is very easily washed free of alkaline material. The liquor drained from the pulp (black liquor) is evaporated to the so-called black ash which is smelted with carbon, when some of the sodium sulphate is reduced to sodium sulphide. The ash is then extracted with water and lime is added to recausticize the sodium carbonate. The black ash may also be smelted with carbon and lime, and the temperature is then kept below 600° C. so that extensive decomposition of the calcium carbonate does not occur. Recovery of the sodium hydroxide by electrolytic methods is possible. Recovery processes are aided if the black liquor is first heated under a pressure of 200atm.; this treatment causes the organic matter extracted from the wood to settle as a tar which is separated from the aqueous liquor.[2,29-49]

Pulps obtained from the calcium bisulphite treatment are purified by a digestion with sodium hydroxide solution; some swelling of the pulp occurs similar to the swelling of cotton fibres in sodium hydroxide. Chemical and electrolytic methods of recovery are applied to these sodium hydroxide liquors.[50-60] A nitric acid process has been operated in Germany for some years. Beech or poplar chips are steeped in 14% nitric acid at a temperature below 50°C., the lignin being oxidized to carboxylic acids and part of the nitric acid being reduced to ammonia. The pulp is purified first by a treatment with chlorine and then by extraction with sodium hydroxide solution which is subsequently recovered.[61] A method of obtaining cellulose from fibrous plants consists in passing the cellulosic material through the cathode compartment and then through the anode compartment of a sodium chloride cell. Thus the raw material is subjected to digestion first with sodium chloride solution and then with a chlorine solution.[62]

In addition to wood, other vegetable matter is used to provide pulp for paper-making. Straw, reeds, esparto-grass and jute and hemp fibres have been used and are pulped by a digestion with sodium hydroxide solution. Frequent exposure of the vegetable material to the air during the digestion process is ensured by suitable agitation of the mixture and a more rapid disintegration of the cellulosic matter ensues. Carboxylic acids are present in the liquor after the treatment.[63-73] A pulp suitable for paper-making can be made from bagasse by digestion first with sodium hydroxide and then with sulphuric acid. As with other pulps, bleaching is effected by chlorine, and if the bleached pulp is given a further treatment with sodium hydroxide solution its characteristics for paper-making are improved. Recovery of the sodium hydroxide from the waste-liquors is effected in the usual ways.[73-81] Japanese Cypress wood treated with 0·5% sodium hydroxide solution is suitable for separators in lead accumulators.[82] Paddy straw soaked in dilute sodium hydroxide solution has better animal feeding value than untreated straw.[83] Sodium hydroxide is also used in the treatment of green olives,[84-86] the clarification of sugar-cane juice,[87] the crystallization of sucrose from certain low-grade sources,[88,89] and in the detection of sugars.[90] It can be used in certain adhesives and cleaner-polishes in conjunction with cellulosic material.[91-93]

Textile Manufacture and Finishing

By far the largest part of the World's output of rayon is made by the viscose (xanthate) process. In outline, the process consists in steeping wood-pulp or cotton linters in sodium hydroxide solution; swelling of the cellulosic material occurs, the liquor is squeezed away, and the pulp is then exposed to the vapour of carbon disulphide (xanthation). The xanthated material is dispersed in more sodium hydroxide solution, and when the dispersion is of the correct viscosity it is spun by being forced through the fine orifices of spinnarets, made of an alloy of platinum. The fine filaments of the viscose solution fall into a setting bath of sulphuric acid as long, thin fibres.[2,94,95] The temperature and other details of the sodium hydroxide solution are of some importance, and the concentration of the solution is closely controlled; in practice it is kept between 10% and 18%. The concentration of impurity cations is kept as low as possible, while the concentration of sodium chloride should not exceed 2%. The viscosity of the viscose solution is markedly affected by the presence of foreign substances.[96-107] In view of the complex nature of the cellulose material, reactions similar to the xanthation reaction have been studied with polyhydric alcohols, such as sucrose, whose constitution is known. Results indicate that the reactions involved are:-

$$ROH + NaOH \rightarrow ROH{,}NaOH$$

$$ROH,NaOH + CS_2 \rightarrow ROCSSNa + H_2O.$$

The number of alcoholic hydroxyl groups per glucose group involved is, however, not known.[108,109] Analysis of some cellulose xanthate preparations made with sodium hydroxide solutions which were rather more concentrated than those usually employed showed a composition corresponding to the formula $C_{12}H_{19}O_9OCSSNa$.[110] The principal by-products of the reaction are sodium carbonate and sodium thiocarbonate; other products such as sodium sulphide are believed to be formed through side reactions.[110-112]

The recovery of the sodium hydroxide from the process is made slightly more difficult than usual by the presence of much organic material, chiefly hemicelluloses, colloidally dispersed in the liquor. Dialysis of the waste solutions is generally accepted, therefore, as an essential preliminary to any chemical treatment.[113-124] Other methods of removing the organic material have been tried; these include shaking the solution with sand, on which the hemicellulose is absorbed, and oxidation of the organic material with inorganic oxides or salts.[125-133] From the clear inorganic liquor sodium hydroxide may be obtained by the causticization process, the various sodium salts being converted first to sodium carbonate which can be treated with the usual causticizing agents.[134-137] The electrolytic methods may also be employed.[138-141] The waste liquors always contain a considerable amount of sodium sulphate from the neutralization of the alkaline viscose solution by the acid spinning bath. This can be converted into sodium chloride by bubbling hydrogen chloride into the solution; crystals of sodium chloride are precipitated, and a pure sodium chloride is subsequently prepared for electrolysis.[142,143] Alternatively, the sodium sulphate solution may be causticized with calcium hydroxide.[144]

It has been known for more than a hundred years that cotton immersed in sodium hydroxide solution undergoes changes that affect the characteristics of the finished fabric, and, in particular, give it a much smoother surface. Moreover, if the cotton fibres are stretched during the immersion the final cloth is highly lustrous. This process of mercerization has acquired considerable importance. Other alkali metal hydroxides cause mercerization, but none are so effective as sodium hydroxide.[145,146] The physical effect of the sodium hydroxide solution is two-fold, a swelling of the fibre and a shortening of the cotton hairs. The extent of the swelling is governed by the concentration of the sodium hydroxide solution, and studies have been made to ascertain whether the swelling is intermicellar or intramicellar.[147-157] Recently it has been discovered that certain micro-organisms may influence the swelling,[158,159] and cellulose subjected to high pressures shows less swelling when subsequently treated with caustic soda.[160] The process of swelling appears to be associated with absorption of the sodium hydroxide by the cellulose fibres, and some studies on the absorption of sodium hydroxide by cotton suggest that compounds such as $C_6H_{10}O_5,NaOH$ or $2C_6H_{10}O_5,NaOH$ may be formed. Measurements of heats of adsorption, however, do not indicate the formation of definite compounds.[161-169] The recovery of sodium hydroxide from the mercerizing process is achieved by the usual methods and may involve dialysis of the solution.[170,171]

The effect of further action of sodium hydroxide solution on mercerized cotton and on linen and rayons has also been examined.[172-177] The bleaching of cotton by the air an alkaline bath has been tried, though there is the possibility that weakening of the cotton fibres may be considerable.[178,179]

Sodium hydroxide is used in vat-dyeing, and the process can be controlled by the amount of sodium hydroxide.[180]

The Action of Sodium Hydroxide on Cellulose

Sodium hydroxide is used with cellulose and ethyl chloride in the manufacture of ethylcellulose. The following reactions are involved (C = cellulose):-

$$C\mathrm{OH} + \mathrm{NaOH} \rightleftharpoons C\mathrm{ONa} + \mathrm{H_2O}$$

$$C\mathrm{ONa} + \mathrm{C_2H_5Cl} \rightarrow C\mathrm{OC_2H_5} + \mathrm{NaCl}.$$

It will be seen that the process is analogous to the formation of ethers from alcohols and alkyl halides, though it is probable that more than one hydroxyl group per cellulose molecule is involved in the etherification process. Very concentrated solutions of sodium hydroxide are used since the rate and the extent of etherification increase with concentration of the sodium hydroxide. If solutions containing more than 50% of sodium hydroxide are used the reactions require temperatures above ambient temperatures. Concentrations as high as 85% of sodium hydroxide may be used, and a more uniformly ethylated product then results. The process is carried out in one operation, the cellulose, ethyl chloride, and sodium hydroxide being mixed in suitable proportions, usually in an autoclave.[1,2,181-185]

The mode of action of sodium hydroxide on cellulose has been much studied. The cellulose is partially soluble in sodium hydroxide solution, and the insoluble residue undergoes swelling (see above). Maximum swelling and maximum solubility occur together in solutions containing about 10% of sodium hydroxide. This also corresponds to a maximum in the electrical conductivity of the solution. The swelling is irreversible and may be due to a number of causes among which osmotic effects, hydration, and penetration of the cellulose by sodium ions have been suggested. The extraction of the hemicelluloses also appears to be at a maximum with solutions containing 10% of sodium hydroxide.[186-196] The different varieties of cellulose behave in different ways towards sodium hydroxide; β-cellulose shows a maximum solubility in 10% sodium hydroxide, but the solubility decreases with more concentrated solutions. With γ-cellulose, however, the solubility increases as the concentration of sodium hydroxide rises up to about 20%. β-Cellulose may be formed from α-cellulose during the extraction from wood-pulp.[197-200]

The results of many workers are interpreted on the basis of the formation of addition compounds of sodium hydroxide and cellulose. Several such compounds have been reported; the formation of any one of them depends chiefly on the concentration of the sodium hydroxide solution. Thus the compound $2\mathrm{C_6H_{10}O_5,NaOH}$ is said to be formed at sodium hydroxide concentrations between 15% and 30%, while at concentrations above 40% the compound $\mathrm{C_6H_{10}O_5,2NaOH}$ is formed. In weaker solutions containing only 4–5% of sodium hydroxide, the compound $12\mathrm{C_6H_{10}O_5,NaOH}$ is thought to be formed from cellulose itself and $6\mathrm{C_6H_{10}O_5,NaOH}$ from mercerized cotton. Other addition compounds reported are $\mathrm{C_6H_{10}O_5,NaOH}$, $3\mathrm{C_6H_{10}O_5,2NaOH}$, and $4\mathrm{C_6H_{10}O_5,3NaOH}$. Cornstarch cellulose forms addition compounds with half, one, and two molecules of sodium hydroxide. Most of the evidence for these compounds comes from absorption studies and from the interpretation of the absorption curve. In addition, it may be remarked that maximum swelling and maximum solubility, which occur in 10% sodium hydroxide solution, correspond to the absorption of one mole of sodium hydroxide per mole of cellulose. The maximum conductivity observed in the same solutions may correspond to the formation of sodium cellulose salts, the cellulose acting as a weak acid.[186,187,195,201-220]

Compound formation is usually accepted as an intermediate stage in the xanthation process.[212,221] X-Ray diffraction examination of cellulose soaked in sodium hydroxide solution shows changes in the pattern of the cellulose; some of the new patterns have been attributed to sodium cellulose compounds.[189,192,208,209,222-225] Some early results of absorption studies were regarded as giving no indication of the formation of sodium cellulose compounds, and the interaction between sodium hydroxide and cellulose was believed to be one of adsorption of sodium hydroxide only. Irregularities in the adsorption curves were attributed to physical or chemical changes in the cellulose.[226-237] More recently, measurements of the heats of reaction between cellulose and sodium hydroxide have been made, and some of the results have been interpreted in terms of the linking of sodium hydroxide into particular parts of the cellulose molecule.[238-240] Ion-exchange measurements show that sodium hydroxide may be bound to amorphous regions of cellulose as well as to crystalline regions.[241] Sodium hydroxide is taken up by cellulose more rapidly from alcoholic solutions than from purely aqueous solutions.[226-228,242,243] The study of the sodium hydroxide-cellulose system has led also to information on the nature of cellulose itself and on the interaction between sodium hydroxide and materials containing cellulose or its derivatives.[244-264] The complex reactions which take place when sodium hydroxide and other reagents act on wood and other vegetable tissue still require further investigation.[265-278]

The Action of Sodium Hydroxide on Wool

Wool fibres absorb sodium hydroxide from solution and undergo some hydrolysis. The reaction is accompanied by swelling of the fibre and, with very concentrated solutions of sodium hydroxide, an increase in the strength of the yarn. Weaker solutions of sodium hydroxide cause considerable disintegration of the yarn. It has been suggested that sodium hydroxide may penetrate into micelles of the fibre.[279-283] Protection against the action of sodium hydroxide is afforded by 1,3-difluoro-4,6-dinitrobenzene.[284] Silk and synthetic polyamide fibres also swell in sodium hydroxide solution, but horsehair contracts.[285-287]

The Refining of Oils

Sodium hydroxide is widely used for the removal of sulphur-containing compounds, chiefly mercaptans, from petroleum distillates and other oils. These compounds are the principal causes of the unpleasant odours of impure varieties of distillates. A number of processes have been described.[288-296] Thus the sodium hydroxide may form sodium hydrogen sulphide, and conditions are so established as to prevent the formation of sodium sulphide.[297] Small amounts of a second substance may be used with the sodium hydroxide; this may be an oxidizing agent such as sodium ferricyanide or sodium hypochlorite, or ethylene oxide which can oxidize the mercaptans to bisulphides.[298-300] Formation of bisulphides, which promotes the purification of the oil, is also achieved by using a mixture of sodium hydroxide and sulphur; the following reaction takes place:-[301]

$$2RSH + 2NaOH + S \rightarrow R_2S_2 + Na_2S + 2H_2O.$$

The sodium hydroxide can be used with cresols or in methanolic solution.[302-304] A physico-chemical study of the purification process shows that it involves a first-order reaction with respect to the carbon disulphide content of the oil and that the rate-determining factor is the diffusion of the carbon disulphide across the oil-water interface. The removal of the carbon disulphide is therefore promoted by effective mixing of the oil and the sodium hydroxide solution and by the use of wetting agents.[305] In addition to removing mercaptans sodium hydroxide neutralizes fatty acids in the oils,[306] and mineral acids in acidified lubricating oils;[307] it also removes ammonia from liquid hydrocarbons extracted from coal-gas.[308]

The recovery of the sodium hydroxide after use is accomplished in several ways. Thus the mercaptans may be extracted with a gas oil in which they are more soluble, or they may be made to form disulphides which are then extracted into naphtha.[309-311] Removal of mercaptans can also be effected by treating the caustic solution with steam or the vapours of steam and alcohol; presumably the sulphur compounds are more volatile under these conditions.[312,313] Finely divided copper, various metal oxides, hydrocarbon compounds of lead, and derivatives of phenol are used in other processes.[314-320] Electrolytic methods involving the anodic oxidation of the mercaptans to bisulphides have also been found successful.[321-324] It has been considered worthwhile to extract naphthenic acids and cresylic acids from these recovery solutions.[325-329] Descriptions of plant used in the refining and recovery processes have been published.[330-332] In addition to its use in the refining of oils, sodium hydroxide is effective as a catalyst in the oxidation of solid paraffin wax.[333]

Sodium hydroxide is also used in the preparation of the catalysts for hydrogenation and dehydrogenation processes.[334-336]

The Extraction, Refining and Finishing of Metals

The best-known extraction process using sodium hydroxide is the Bayer process for the extraction of alumina from bauxite. The effectiveness of sodium hydroxide in dissolving aluminium oxide appears to depend partly on whether the latter is present as gibbsite, boehmite, or hydrargillite.[337] Loss of sodium hydroxide in the waste liquors can be a serious economic factor in the process, and recovery of sodium hydroxide is important.[338,339] The abundance of aluminium in silicate rocks has led to the investigation of methods of winning the metal from these sources but the resistance of silicates to chemical attack limits the extent of extraction of the aluminium. Thus kaolinite digested at 200°C. in an autoclave with 36% sodium hydroxide solution is only partially decomposed.[340] The lime-soda sintering process is used with success, while attack on aluminous shales with sodium hydroxide at 600-700°C. renders most of the aluminium oxide soluble, though shales of the kaolinite type give the least satisfactory results.[341,342] The action of sodium hydroxide on minerals of the spinel type has also been studied.[343]

Solutions of sodium hydroxide are also used in the extraction of magnesium from sea-water,[344] tungsten from scheelite,[345,346] and thorium from monazite;[347] they are also used in the refining of gold by the amalgamation process,[348] in the separation of cerium from other rare-earths,[349] and in the concentration of pyrite and arsenopyrite by flotation methods.[350] When zinc ores are leached with concentrated solutions of sodium hydroxide, sodium zincate is formed from which the zinc can be obtained by electrolysis.[351] Sodium hydroxide is used for the solution mining of potassium salts.[352] Niobium and tantalum can be obtained from columbite and zirconium from zircon by treatment of the ores with fused sodium hydroxide at high temperatures.[353-355] Phosphate rocks may be digested with sodium hydroxide solution in the manufacture of fertilizer.[356-358] In the extraction of iodine from sodium iodate liquors, iodine can be displaced from the iodate by bromine or chlorine in sodium hydroxide solution.[359] Sulphur is more thoroughly removed from pyrites if sodium hydroxide or some other material is added to the pyrites so that it forms a uniform and granular powder when heated.[360] The ash-content of natural graphite can be reduced by treatment with fused sodium hydroxide at a red heat.[361] Coal may be oxidized with oxygen and sodium hydroxide, and carboxylic acids obtained among the products.[362]

The phosphorus-content and sulphur-content of steels can be lowered by adding sodium hydroxide to the molten steel; haematite or lime may be added at the same time. An oxidizing atmosphere is essential to ensure the removal of phosphate and sulphate in the slag.[363-369] Sodium hydroxide can also be used in various processes to improve hardness, corrosion resistance, and mechanical working of steel and iron.[370-373] In the refining of lead by the Harris process, lead bullion is treated with molten sodium hydroxide and other sodium salts, whereby arsenic, tin, antimony, and other impurities are converted to their sodium salts; the melt is leached with water and the impurities extracted from the solution in various ways.[374,375] Lead or its alloys may also be refined by adding a mixture of sodium hydroxide and sulphur to the molten metal; a dross containing the impurities–iron, copper, nickel, arsenic and sulphur–forms on the surface of the molten metal.[376] A solvent-extraction process involving molten lead and molten sodium hydroxide, which are immiscible, has also been described.[377] Other processes using sodium hydroxide include those for the manufacture and finishing of titanium,[378,379] and the removal of tellurium from antimony.[380]

The surface finishing of metals is important not only in providing a pleasing clean surface, but also because it may have a bearing on the subsequent corrosion of the metal. In the removal of surface films of oxides, of impurities not removed in the extraction, and of grease, sodium hydroxide, either in solution with other substances or molten and anhydrous, has proved effective.[381-387] Sodium hydroxide, alone or with other substances, may cause corrosion of many metals, and it is useful as a means of testing so-called non-corrodible surfaces.[388-398] The problem of intercrystalline corrosion, which leads to "caustic cracking" in mild steels, has been discussed elsewhere (see page 699), but the problem is important in other respects also.[399,400] Under certain conditions sodium hydroxide can be used as a corrosion inhibitor; mixed with arsenious oxide it is fed to oil-wells and corrosion of the oil-pipe is reduced. A spray of sodium hydroxide solution reduces rusting in compressed-air lines.[401-408] Stainless steel may undergo surface pitting in aerated solutions containing chloride ions, and this can be partly prevented by the addition of sodium hydroxide.[409-412] Corrosion may be inhibited by the formation of oxide films on the surface of a metal, and for this purpose sodium hydroxide solutions are sometimes effective, especially with steels.[413-418] A protective coating can be formed on metal surfaces by exposing the metal to the vapours of sodium hydroxide and sodium fluoride at about 750–800°C. and subsequently annealing the metal.[419] Electroplating and electropolishing may be done in alkaline solution; a tin-zinc alloy deposit formed from an alkaline bath has good corrosion resistance.[420-422] A coating of zinc on iron is less tenacious if the iron has previously been passivated with sodium hydroxide solution than if it has been treated in other ways.[423] Solutions containing sodium hydroxide, sodium cyanide, and *m*-nitrobenzoic acid are recommended for the chemical stripping of electroplated deposits.[424] Ancient bronze articles can be cleaned if they are made the cathodes in a bath of 2% sodium hydroxide solution through which a small current is passed; oxides and basic carbonates are reduced without being stripped off the metal. The diameter of tungsten wire can be reduced beyond the limits of mechanical wire drawing by dissolving the outer layers of thin wire in solutions containing potassium ferricyanide and sodium hydroxide.[426]

Glass, Ceramic and Related Industries

The thixotropic behaviour of bentonite suspensions is affected by the addition of sodium hydroxide owing to adsorption and the formation of various sodium bentonites.[427-433] These investigations contribute usefully to the study of the colloidal nature of clays. It is of particular interest to examine the causes and mechanism of the flocculation and deflocculation of clay sols.[434-440] Thus deflocculating agents are important in the preparation of "clay slips," or suspensions used in ceramic manufacture, and the choice of the deflocculating agent may affect not only the viscosity, pH, and other properties of the slip, but also some of the characteristics of the finished ceramic body. Among the deflocculating agents used, sodium hydroxide is found to be fairly satisfactory.[441-446] Sodium hydroxide is also used in the manufacture of enamels and glazes.[447-449] Certain well-drilling fluids contain lime, quebracho, and sodium hydroxide, the last being used, partly at least, to maintain a high pH in the slurry and to control the viscosity.[450,451] The absorptive properties of certain clays such as kaolinite and montmorillonite have been studied by cation-exchange methods with sodium hydroxide.[452-455]

Sodium hydroxide is used in the manufacture of certain cements. Small amounts of it increase the rate of hardening of the concrete. It also increases the rate of wet-grinding of raw materials in cement manufacture. It may be used in the manufacture of bricks and in a heat-insulating concrete. The presence of sodium hydroxide in cements is not always advantageous, as it may affect adversely some of the characteristics of the concrete, while cements that have been immersed in sodium hydroxide solutions lose their tensile strength.[456-468] Sodium hydroxide can be used in aqueous solution to remove iron oxide from sand.[469] Mixed with lignosulphonic acid and various organic colouring agents it can be used to impart a colour to woven glass fibres, the fibres being immersed in a boiling aqueous solution of the mixture.[470] Sodium hydroxide increases the rate of deterioration of glass surfaces.[471-474]

Cleaning Agents

Sodium hydroxide is used as a "builder" in soaps and as a constituent of some detergent preparations.[475-485] The viscosity of soap solutions is increased by the addition of sodium hydroxide.[486] The effectiveness of commercial detergents can be estimated by comparing their cleaning action with that of sodium hydroxide under standard conditions.[487] Sodium hydroxide solutions are used as cheap cleaning materials in bottle washing plants; for this reason the action of sodium hydroxide solutions on glass has been studied.[471-474,488-494] It is also used for cleaning evaporators in sugar refineries.[495] Mixed with other sodium salts it can be used for degreasing metals; abrasive action can be provided by adding powdered aluminium or some of the more common abrasives to the alkaline cleaner.[387,496-500] A concentrated solution of sodium hydroxide will remove tarry deposits from metal surfaces.[501] The effectiveness of sodium hydroxide as a detergent for metal cleaning has been studied by a radioisotope method.[502]

Solutions of sodium or potassium hydroxide in ethanol or methanol are effective as low-temperature cleaning materials.[503] Addition of sodium hydroxide and sodium silicate prevents precipitation of hydrogen peroxide bleaching baths.[504,505]

Plastics and Other High Polymers

The polymerization of formaldehyde to form paraformaldehyde is catalyzed by sodium hydroxide.[506,507] It also appears to be the best alkaline catalyst in the formation of resins produced by the condensation of formaldehyde and phenol or substituted phenols, though it is reported to be inferior in some respects to the alkaline earth hydroxides.[508-511] The condensation of phenols with furfural is also catalyzed by sodium hydroxide,[512,513] though other substances, including acids, alkalies and salts, may serve the same purpose. Use is made of sodium hydroxide in the finishing stages of the production of phenolic resins, polystyrene polymers and polyester plasticizers.[514-516] In the production of synthetic rubbers, sodium hydroxide is used as an accelerator,[517,518] as a stabilizer of the latex,[519] and to facilitate the dispersion of carbon black.[520] Sodium hydroxide is reported to be the best accelerator in the polymerization of dihydroxydimethylsilane, but it also accelerates the pyrolysis of methylsilicone resins.[521,522]

Sodium hydroxide has been used, together with many other substances, in investigations of the durability and resistance to chemical action of various plastics. Thus polyvinyl chloride plastics and fibres are highly stable to solutions of sodium hydroxide,[523-528] but bakelite (phenol-formaldehyde resin) is gradually corroded by dilute sodium hydroxide solution in the cold.[529] Embrittlement, leading to stress corrosion, results when polymethylmethacrylate resins are exposed for a sufficiently long time to 20% sodium hydroxide solution.[530] Changes in flexibility of melamine–formaldehyde and melamine-urea resins occur after they have been treated with dilute sodium hydroxide solution.[531] The action of sodium hydroxide on nylon and terylene fibres has also been examined.[532-534].

Miscellaneous Uses of Sodium Hydroxide

Sodium hydroxide is, or has been, used in a number of manufacturing processes in addition to those already mentioned. They include the production of hydrogen peroxide,[535] the production of oxygen,[536] the electrolytic production of sodium,[537,538] the production of hydrazine,[539] the hydrogenation of carbon monoxide,[540,541] the production of phenol from coal,[542,543] the production of glycerol,[544] of pentaerythritol,[545,546] and sodium formate,[547] the hydration of ethylene oxide,[548,549] the production of tetrafluoroethylene,[550] and of dyes,[551,552] and in photographic developers.[553] The addition of about 2% of caustic soda to bituminous coal affects the yield of pitch in low-temperature carbonization.[554,555] During the process of carbonization the coal first becomes plastic and then cokes; both these stages can be advantageously influenced by the addition of sodium hydroxide to the coal.[556,557] The ash-content of certain coals can be reduced to less than 1% if the powdered coal is heated with fairly concentrated caustic soda solution in an autoclave.[558] The carbonization of wood is also affected by sodium hydroxide as well as by other chemicals.[559] The use of sodium hydroxide for softening boiler-feed water has been recommended, especially for waters containing certain proportions of bicarbonate and sulphate.[560-563] The pH of boiler-feed water can be adjusted with sodium hydroxide.[564] Gases are effectively dried with caustic soda, and flaked caustic soda has been particularly recommended for the purpose.[565-567] An absorbent for carbon dioxide, containing less than 0·001% of carbon dioxide, and suitable for work with radioactive carbon, can be made with sodium hydroxide.[568] A low-pressure hydrogen generator suitable for filling ballons used for meteorological work utilizes a solution of sodium hydroxide and aluminium or some other suitable material.[569]

Sodium hydroxide is one of a number of substances that cause swelling of leather and pigskin and facilitate the removal of hair from fresh hides.[570-574] Addition of sodium hydroxide to chromium salt solutions affects certain stages in the tanning process.[575,576] A solution of lime, lead oxide, sodium carbonate and sodium hydroxide is claimed to straighten curled hair.[577] Mixtures of sodium hydroxide and naphthalene are preservatives for pigskin, though naphthalene alone is reported to be superior to any of the mixtures.[578] The ethanolysis of a number of vegetable oils results in the formation of glycerol, and the reactions are catalyzed by sodium hydroxide. The catalyst is eventually consumed as it forms a soap with the oil.[579-586] Sodium hydroxide catalyzes similar reactions with cuttle-fish oil,[587] and affects the hydrogenation of whale-oil.[588] The use of sodium hydroxide has also been studied in the treatment of haemoglobin,[589] fibrinogen,[590] chitin,[591] pituitary extracts,[592] a number of proteins,[593-596] and in processes designed to make meat more tender.[597] Sodium hydroxide, or preparations including it, have been tried as weed-killers,[598,599] while mixed with tar and phenol it forms a fertilizer rich in humic acid and humates.[600] It can also be used in detecting insect infestation of wheat.[601] In making up liniments, good emulsification is achieved if sodium hydroxide, among a number of substances, is added to the mixture in suitable amount.[602]

Various mixtures containing sodium hydroxide are suitable as paint or varnish removers,[603,604] while sodium hydroxide, alone or with hydrogen peroxide, is used with sodium silicate to erase printing ink.[605,606] Sodium hydroxide may be employed in the preparation of an adhesive containing aluminium citrate or tartrate,[607] and with a borate and a phosphate to prepare washes for coating the insides of moulds.[608] Sodium hydroxide is used with other materials, chiefly silicates, for lubricating extrusion presses,[609] while pure sodium hydroxide is useful as a standard in lubrication measurements.[610] A dilute solution of sodium hydroxide is used in sealing tanks containing hydrogen chloride or chlorine.[611] It is used as the electrolyte in primary cells;[612] the consumption of carbon anodes has been studied during electrolysis of dilute sodium hydroxide solution.[613] The eutectic mixture of anhydrous sodium hydroxide and potassium hydroxide is recommended fo heat transmission at high temperatures, above 600°C.[614] A solution of sodium hydroxide is an effective fire-extinguisher.[615] The addition of concentrated hydrogen peroxide to a concentrated solution of sodium hydroxide causes the formation of a colloidal foam.[616] Sodium hydroxide is used to control the pH of radioactive waste liquors.[617]

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SECTION XXX

SODIUM FLUORIDE

By W.E. GREEN

Formation

Sodium fluoride has been detected in 'smog' particles at Los Angeles,[1] where it probably originates from the effluent gases of industrial processes. It has been shown to escape during the smelting of fluorine-containing vitreous enamels.[2]

Study, by means of *X*-ray diffraction, of the interaction taking place when mixtures of sodium chloride and potassium fluoride are fused together shows that, in these conditions, the reaction $KF + NaCl \rightleftharpoons NaF + KCl$ proceeds completely from left to right.[3] Pure sodium fluoride may be obtained by heating sodium fluosilicate to its melting point.[4] Decomposition of sodium fluosilicate to form sodium fluoride is said to proceed in the range 315°–370°C.[5] A laboratory method for the preparation of the pure salt depends on precipitation of fluosilicate (present as the main impurity) by addition of solid potassium chloride to a saturated solution of commercial sodium fluoride; complete removal of fluosilicate is confirmed by adding phenolphthalein and one drop of 0·1N sodium hydroxide solution to the fluoride solution and boiling; if fluosilicates are absent the pink colour remains. The filtered solution is then evaporated and crystallised.[6]

The increased technical importance of sodium fluoride has produced a fairly considerable body of literature, mainly patents, on its preparation. Commercial preparation in the wet way from sodium carbonate and hydrofluoric acid has been described in some detail. The sodium fluoride thrown out of solution is contaminated with the acid salt and with fluosilicate; to eliminate these it is necessary to treat the slurry with more sodium carbonate until it gives a distinct red colour with phenolphthalein and then to heat with live steam to ensure neutralisation of acid fluoride and decomposition of fluosilicate.[7] A patented process makes use of the interaction of gaseous hydrofluoric acid with heated solid sodium carbonate to produce either the neutral or the acid salt.[8] Hydrofluoric acid can also displace hydrochloric acid from solid sodium chloride, giving the neutral salt at temperatures between 80°C. and 120°C. and the acid salt at room temperature.[9] From aqueous solutions[10,11] or suspensions[12-14] of sodium chloride, addition of hydrofluoric acid yields acid sodium fluoride. The neutral salt may be obtained from solutions of sodium chloride or nitrate by the simultaneous addition of hydrogen fluoride gas and ammonia solution.[15]

A number of modifications have been developed of the Berzelius method of alkali hydrolysis of the fluosilicate (Mellor, II, 512); for example, sodium hydroxide may be used to dissolve the silica set free in this reaction and thus to separate it from the less soluble sodium fluoride.[16-18] Because sodium fluoride is much less soluble in water than the potassium salt, the same type of process may be used to make sodium fluoride from potassium fluosilicate.[19-22] Ammonia will act upon sodium fluosilicate in a similar way to form a mixture of ammonium and sodium fluorides, which is subsequently treated with sodium chloride to recover all the fluoride as the sodium salt.[23]

Sodium fluoride of low silica content may be obtained by the action of sodium hydroxide or carbonate on fluoboric acid, made by treating a mixture of fluorspar and boric acid with sulphuric acid.[24]

Fusion of fluorspar with sodium carbonate and subsequent extraction of sodium fluoride with water has been examined in some detail. The reaction $CaF_2 + Na_2CO_3 \rightleftharpoons 2NaF + CaCO_3$ appears to proceed quantitatively from left to right, but extraction of the sodium fluoride by water is reduced, it is believed, by formation of an insoluble double compound Ca_2SiC_4,NaF, deriving from the silica present in the fluorspar. Addition of ferric oxide to the reaction charge is said to suppress the formation of this complex, with the result that sodium fluoride can be recovered in 94% yield.[25] Several patents have been based on the direct opening up of fluorspar with sodium carbonate,[26-29] or with potassium carbonate; in the latter case sodium carbonate is added to the aqueous extract to precipitate sodium fluoride.[30-31] Fluorspar may also be decomposed by prolonged heating with concentrated aqueous sodium hydroxide.[32]

Properties

Sodium fluoride crystallises in the cubic system and has the rock-salt structure; the lattice constant a is 4·6344 A.[33]

Although sodium fluoride normally crystallises from aqueous solution in cubes, the presence of substances yielding hydroxyl ions promotes the formation of octahedral crystals, because of absorption of hydroxyl in place of fluoride ion at the crystal surface. The presence of substances which form double salts with sodium fluoride may also affect the crystal habit by preferential absorption along planes consistent with the structure of the double salt.[34] In the absence of impurities, rate of evaporation may also determine the crystal shape; slower rates favour formation of cubic crystals, whereas above a certain critical rate octahedra are formed.[35]

Redetermination of the density at 18°C. gave a figure of 2·726, from which the molecular volume is calculated to be 15·41.[36] The same author in a later paper quotes a density at 0°C. of 2·804.[37] Calculation from X-ray data gives a density of 2·802.[33]

The compressibility, from determinations made on aggregates of small crystals, is:-

$$\text{at } 30°\text{C., } \delta V/V_0 = (20{\cdot}7 \times 10^{7})\, p - (17{\cdot}7 \times 10^{12})\, p^2;$$

$$\text{and at } 75°\text{C., } \delta V/V_0 = (20{\cdot}8 \times 10^{7})\, p - (18{\cdot}1 \times 10^{12})\, p^2$$

where p is the pressure in kg./sq. cm.[38]

The cubic coefficient of expansion is 98×10^{-6} at −40°C. and 68×10^{-6} at −131°C.[37] The specific heat between 300° and 800°C. is given by the expression $0{\cdot}2474 + (1{\cdot}88 \times 10^{-4})t + (2{\cdot}53 \times 10^{-8})t^2$.[39]

A fairly recent American source gives the melting point of sodium fluoride as 995°C.,[40] while some Russian sources quote 990°C.,[41] and less recent German determinations 988°C.[42] and 993°C.[43] The latent heat of fusion is quoted as 7800g.-cal./mole, and from this the entropy of fusion is calculated as 6·17; on the assumption that the entropy of fusion should be $\frac{3}{2}R$ when an ion is formed, this result is taken to indicate almost complete dissociation of sodium fluoride on fusion.[44]

Freezing point equilibria have been investigated for a number of systems involving sodium fluoride. Metallic sodium and the fluoride are mutually soluble in the molten state, the solubilities rising rapidly to a consolute point estimated to occur at 1100°C., when 30 mol.-% of the fluoride is dissolved in the metal. A monotectic exists at 990°C., (5°C. below the melting point of the pure salt), and at this temperature the solid salt contains approximately 1 and the liquid salt approximately 2 mol.-% of the metal, while the liquid metal contains 17 mol.-% of the salt.[40] Eutectic temperatures and compositions for some binary

TABLE I. - BINARY SYSTEMS CONTAINING SODIUM FLUORIDE

Second Component	Eutectic		Reference
	Temp. °C.	Mol.-% NaF	
Sodium chloride	675 670 680	27·5 34·5 28	Mellor II, 514 45 46
Sodium iodide	603	18	41
Sodium carbonate	690	40	45
Sodium nitrate	304	3·5	47
Sodium disilicate	797	39·5	48
Sodium metasilicate	913	28·5	49
Sodium tetraborate	680	20	50
Sodium chromate	646 642	21 10·5	51 52
Sodium phosphate	734	-	53
Potassium fluoride	700 710	40 40	Mellor II, 514 41
Potassium chloride	653 630	19 18	54 46
Potassium iodide	631	12	41
Potassium carbonate	568	34	55
Potassium chromate	730	30	51
Potassium sulphate	718	40	56
Aluminium fluoride	885	86	57
Barium titanate	952	93	53

mixtures are given in Table I.

The mixtures of sodium fluoride with potassium salts are simple binary systems, there being no metathesis between sodium fluoride and these salts. The corresponding sodium salts react completely with equimolecular proportions of potassium fluoride to form sodium fluoride,[3,56,58] and non-stoicheiometric proportions thus form ternary systems in which all the fluoride or all the sodium, whichever is the least, is combined as sodium fluoride. The general picture is thus presented of a phase diagram separated by the stable diagonal NaF-KX into two ternary systems NaF-KF-KX and NaF-NaX-KX. Several such systems have been studied, including [Na,K | F,Cl][46,58] [Na,K | F,Br],[59] [Na,K | F,I],[41,56] [Na,K | F,NO_3],[47] [Na,K | F,CO_3],[55] [Na,K | F,B_4O_7],[50] and [Na, K | F,CrO_4].[51] With these it is possible to produce fluid compositions stable over wide ranges of temperature, and some will be referred to again in the applications of sodium fluoride.

Several independent determinations of vapour pressure have been made which agree well with one another; the figures in Table II represent the most complete series of determinations.

The same authority gives the boiling point as 1705°C. and the calculated heat of vaporisation as 51·1kg.-cal. per g.-mol. Another worker, from experimental data on vapour pressures between 750°C. and 1000°C., gives the equation $\log p = -11387{\cdot}7/T + 8{\cdot}654$ and the extrapolated boiling point as 1702°C., with a heat of evaporation of 51·9 kg.-cal. per g.-mol.[61]

The dielectric constant of sodium fluoride, determined by Starke's method, is reported as 6·00,[62] and the electric strength, in terms of the field value at which electron energy suddenly increases and ionisation sets in, has been determined as $2{\cdot}4 \times 10^6$V./cm.[63] Transport-number determinations show that increasing temperature changes solid sodium fluoride from a pure cation conductor to a bipolar conductor (see Table III). On the other hand, an earlier group of workers,[65] working with discs made from compressed powder, decided

TABLE II.- VAPOUR PRESSURE OF SODIUM FLUORIDE[60]

Temp. °C.	*p*, mm.	Temp. °C.	*p*, mm.
1426	87	1622	420
1456	110	1641	483
1492	155	1655	531
1536	207	1665	575
1541	215	1669	587
1562	267	1677	635
1597	356	1701	756

TABLE III.- TRANSPORT NUMBERS IN SOLID SODIUM FLUORIDE[64]

Temp. °C.	*n*, cation	*n*, anion
550	0·995	0·004
600	0·916	0·814
625	0·861	0·139

that the fluoride ion played no part in conduction below 800°C. The electrical conductivity of the fused salt at 1000°C. is reported as 5·52ohm^{1} cm.$^{-1}$,[66] though some earlier investigators give figures of 3·15 at 1000°C., rising to 3·48 at 1040°C.[67] The decomposition potential of the fused salt, calculated from thermodynamic data, is given as 4·4 to 4·6V. at 950°C.,[68] while measurements based on breaks in the current-potential curve in a special graphite cell gave the results in Table IV.

TABLE IV. - DECOMPOSITION POTENTIAL OF FUSED SODIUM FLUORIDE[69]

t, °C.	*E* (V.)
860	2·95
920	2·80
968	2·63
1022	2·45

It should be noted, however, that the first three readings represent temperatures well below the accepted melting point of sodium fluoride. An earlier worker[70] obtained much lower figures, from 0·96V. at 827°C. to 0·58V. at 917°C.; mixtures of sodium fluoride and potassium chloride were used to lower the melting point and to suppress anode effect.

The refractive index (n_D) is 1·336.[71] Examination of the transmission of light in the extreme ultra-violet by sodium fluoride showed it to be transparent down to 1320A., which was thought by the investigators not to represent the limit for the transparency of the pure salt.[72]

The heat of formation of sodium fluoride has been reported as 136·2 kg.-cal.;[73] this figure is based on direct determination of the heat of formation of hydrogen fluoride by combination of the elements, and on the reaction $\frac{1}{2}F_2$ + NaCl (solid) = NaF + $\frac{1}{2}Cl_2$ (gas). A later figure, said to be based on a critical survey of the literature since 1938, is 136·6 kg.-cal./g.-mol.[4]

Values of the solubility of sodium fluoride in water are given in Table V.

The heat of solution, corrected to infinite dilution, is 213 ± 10 g.-cal./g.-mol.;[75] the sum of the standard free energies of hydration of the ions Na^+ and F has been calculated as 197 kg.-cal./g.-mol.[76]

In aqueous solutions of hydrofluoric acid at 20°C., the solubility shows at first a slight rise with increasing acid concentration, the solid phase being sodium fluoride. At higher acid concentrations the stable solid phase is sodium hydrogen fluoride and the solubility falls off. At the triple point the solution contains 0·48g. of hydrogen fluoride and 4·55g. of sodium fluoride per 100g.

TABLE V. - SOLUBILITY OF SODIUM FLUORIDE IN WATER[74]

t, °C.	Solubility g.mol./1000g. water	Density (ρ_4^t) (saturated solution)
0	0·871	-
25	0·983	1·0384
35	0·989	1·0354

TABLE VI. - SOLUBILITY OF SODIUM FLUORIDE IN AQUEOUS HYDROGEN FLUORIDE AT 20°C.[77]

g./100g. water			g./100g. water		
Hydrogen Fluoride	Sodium Fluoride	Solid Phase	Hydrogen Fluoride	Sodium Fluoride	Solid Phase
0·081	4·14	NaF	0·660	3·45	$NaHF_2$
0·104	4·19		0·831	2·99	
0·135	4·23		1·16	2·46	
0·420	4·51		1·20	2·49	
			1·55	2·20	
0·473	4·58	NaF $+NaHF_2$ (triple point estimations)	2·22	2·04	
0·483	4·58		2·50	2·00	
0·485	4·56		2·70	2·01	
0·492	4·54		4·17	1·88	
0·496	4·50		10·28	1·79	

of water. The complete solubility figures are given in Table VI.

The solubility of sodium fluoride in liquid hydrogen fluoride is 30·1 ± 0·1g. per 100g. of solvent at 11°C., 25·1 ± 0·1 at -9·8°C. and 22·1 ± 0·1 at -24·3°C.[78] In aqueous sodium hydroxide solutions, the solubility of sodium fluoride has been shown to vary inversely with the concentration of hydroxide and, as with pure aqueous solutions, to vary only slightly with temperature.[79] In aqueous hydrogen peroxide, sodium fluoride is more soluble than in water, the solubility rising rapidly with increasing concentration of hydrogen peroxide.

TABLE VII. - SOLUBILITY OF SODIUM FLUORIDE IN AQUEOUS HYDROGEN PEROXIDE AT 25°C.[80]

Hydrogen Peroxide, %	Sodium Fluoride g.-mol./1000ml.
0	0·9989
15·72	1·216
31·43	1·457

The solubility in hydrogen peroxide solutions is also more dependent on temperature than that in aqueous solutions.[81] In bromine trifluoride the solubility at 25°C. is 2·55g./100g.[82] Solubility in ethanol/water mixtures decreases with increasing alcohol content to a minimum at about 50% of alcohol.[83] 100g. of carefully dried methanol dissolves 0·041g. of the salt.[84] In liquid sulphur dioxide, the solubility is said to be in the range 0·01–0·10%.[85]

Investigation of mixed solutions of sodium fluoride with other salts has revealed no evidence of double-salt formation with sodium chloride, though with sodium sulphate a double salt Na_2SO_4,NaF is formed.[86] No double salts are formed with ammonium fluoride[87] or with sodium tetraborate solutions.[88] In the system sodium fluoride–boric acid–water at 25°C. there is some evidence of complex formation in solution, as each solute increases the solubility of the other considerably; the eutonic solution contains 44·34% of boric acid and 12·63% of sodium fluoride.[89]

The equivalent conductivity at infinite dilution has been reported as 90·1.[90] Attempts to determine the decomposition potential of sodium fluoride in aqueous solution have been unsuccessful; although breaks were observed in the potential curve, no true decomposition potential could be established.[91]

Aqueous solutions of sodium fluoride appear to have little effect on borosilicate glass, even after prolonged storage, though soda-lime glass shows definite signs of attack.[92] In the hydrothermal growth of quartz from vitreous silica at high temperatures and pressures, the presence of small amounts of sodium fluoride dissolved in the water has been shown to promote rapid and extensive growth of the quartz crystal. It has been shown that the greater part of the fluoride ion is converted to fluosilicate ion, and it is suggested that the hydroxyl ion made available by the reaction $6F^- + SiO_2 + 2H_2O = SiF_6^{2-} + 4OH^-$ may react further with vitreous silica, as in the reaction $2OH^- + SiO_2 = SiO_2(OH)_2^{2-}$.[93] Thermochemical calculations indicate the possibility of hydrolysis of sodium fluoride, but only at high steam pressures. The hydrolytic stability of the fluoride is said to be less than that of the other sodium halides.[94]

Sodium fluoride can absorb hydrogen fluoride from gases at temperatures up to about 125°C., forming sodium hydrogen fluoride, which may be decomposed again by heating to 300°C.[95] Absorption of silicon tetrafluoride by sodium fluoride to form sodium fluosilicate has been studied over a range of temperatures. Combination is slow below 200°C., becoming more rapid at about 240°C. At higher temperatures, between 315° and 370°C., the fluosilicate decomposes again to form sodium and silicon fluorides.[5]

Investigation of the mechanism of removal of fluorine from sodium fluoride solutions by calcium compounds indicates that calcium oxide and sulphate remove the fluorine by double decomposition until the concentration of fluoride ion in the solution corresponds to the solubility of calcium fluoride. Calcium carbonate removes fluorine from solution by ionic adsorption, in accordance with the Freundlich adsorption isotherm.[96] Sodium fluoride can be made to react with calcium carbonate, in the presence of a small amount of water, at elevated temperatures under pressure. The presence of carbon dioxide assists the reaction.[97] In the temperature range 500°-800°C. sodium fluoride reacts completely with the oxides of calcium, strontium and barium to form the alkaline earth metal fluoride and sodium oxide. With magnesium and zinc oxides, on the other hand, double fluorides are formed, e.g., $3NaF + MgO = Na_2O + NaMgF_3$.[98]

When sodium fluoride is heated to 650°-750°C. in air with an equimolecular proportion of sodium metaphosphate, fluorine is said to be evolved according to the equation:

$$2NaF + Na_2P_2O_6 + \tfrac{1}{2}O_2 \rightarrow Na_4P_2O_7 + F_2.$$[99]

In the fused state, sodium fluoride is effective in depolymerising sodium polyphosphates.[100]

Under the influence of ultra-violet irradiation, halogen interchange can be made to take place between aliphatic halides and sodium fluoride to form aliphatic fluorine compounds.[101] A method for preparation of benzoyl fluoride is based on a catalysed reaction between sodium fluoride, phenyl chloride, and carbon monoxide under pressure.[102]

Applications

Reference to the literature on freezing-point equilibria shows that sodium fluoride enters into a number of systems useful because of their melting points. Systems including sodium fluoride with the chlorides, carbonates, borates, and chromates of sodium and potassium, for example, offer compositions melting in some cases below 600°C. and stable over a wide range of temperatures. Such compositions have been suggested as salt baths for the heat treatment of metals[45,50,51,55,103] and as melting and refining fluxes,[54,104] as well as in soldering and welding. Synthetic cryolites and other mixtures containing sodium fluoride and aluminium fluoride are of importance in the electrowinning and electrorefining of aluminium. A double fluoride of sodium and beryllium, mixed with barium fluoride, has been used in the production of beryllium by fusion electrolysis.[105] Sodium fluoride, mixed with the chloride to lower the melting point, has been found effective as a flux in the removal of magnesium from aluminium–magnesium alloys.[106]

The fluxing action of sodium fluoride finds application in the ceramics and glass industries. In glass and in vitreous enamels it also functions as an opacifier, the mechanism of which, while not yet fully explained, is thought to involve formation of highly dispersed crystalline phases.[107] *X*-Ray diffraction has established that sodium fluoride is freely precipitated from the melt alone or as a double fluoride.[108] Sodium fluoride additions also decrease the colour in glass due to iron, particularly in the presence of oxidising agents.[109,110] Glasses have also been produced in which sodium fluoride is one of the major glass-forming constituents;[111,112] these glasses are characterised by low refractive index and low dispersion.

As a mineraliser in the burning of cement, small additions of sodium fluoride are effective in reducing the time taken for complete fixation of calcium oxide.[113,114] 'Dusting' of dicalcium silicate bricks is prevented by addition of sodium fluoride as mineraliser.[115] Study of the calcination of hydrated aluminas has shown that up to 5% of sodium fluoride lowers the temperature at which hydrargillite is transformed (through boehmite) into α–alumina.[116] A fused mixture of sodium fluoride and phosphate has been suggested as a medium for the growth of barium titanate monocrystals.[53]

Mention has been made, in discussing the properties of sodium fluoride, of the manner in which it promotes the hydrothermal growth of quartz crystals. It has been found that the presence of sodium fluoride and hydroxide in solution, in sufficient amount, makes it possible to replace 'melting-quality' quartz as the raw material by mineral forms of silica such as flint and quartzite.[117]

A number of uses or suggested uses for sodium fluoride are based on its toxicity towards insects, fungi and other lower forms of life. Its effectiveness as a preservative against decay of timber has been established for some years,[118,119] factors militating against its use being cost and the ease with which it is removed from timber exposed to the elements, as in railway sleepers. A mixture with potassium chromate and methanol is said to be used for impregnating mine timbers.[120] It is also effective against insects that attack wood.[121,122] A systematic study has suggested that its effectiveness against lower organisms depends on their low calcium content, which is precipitated from the tissues as calcium fluoride.[123] Other suggested uses include mothproofing,[124] control of chicken lice[125] and cockroaches,[126] and as a preservative in cold-sizing materials.[127]

Much has been written on the relationship between fluorine deficiency in drinking water and the incidence of dental caries, and methods have been worked out for dosing public water supplies with fluorine compounds, including sodium fluoride, in areas where the natural fluorine content is considered to be too low.[128] The use of sodium fluoride as an ingredient in the dentifrice has also been proposed.[129]

In aqueous solutions, small concentrations of sodium fluoride are effective as corrosion inhibitors for iron, zinc and cadmium,[130] and aluminium,[131] and it is used in conjunction with phosphates, chromates and other anions

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to produce corrosion-resistant films on these metals.[132,133] A mixture of the vapours of sodium fluoride and sodium hydroxide is used for a similar purpose in the atmosphere of a bright annealing furnace.[134]

As an addition agent in chromium-plating baths, sodium fluoride improves current efficiency and widens the bright plating range.[135] It has also been proposed in zinc-plating baths[136] and in the chemical plating of nickel from hypophosphite baths.[137]

The presence of a small amount of sodium fluoride has been found to promote nitrogenation of calcium carbide.[138] Soaps have been developed for use in hard water or in sea water, containing sodium fluoride present in such a form that it dissolves in water more readily than the soap, forming complexes with those anions present in the water which would otherwise form insoluble compounds with the soap.[139] Treatment of soil linings for canals, water reservoirs, etc., with sodium fluoride is said to reduce their permeability to water by precipitation of calcium fluoride.[140]

Double Salts of Sodium Fluoride

Sodium hydrogen fluoride, $NaHF_2$, can be formed in several of the processes by which the neutral salt is made. It is formed by the action of hydrogen fluoride upon the normal salt in aqueous solution (see Table VI, p. 744) or in the solid state.[95] It crystallises in the hexagonal system, and the lattice constants are a_0 = 3·468 and c_0 = 13·76A., the density calculated from the *X*-ray data being 2·16.[33]

Reference has already been made to the formation of sodium fluosilicate by the action of silicon tetrafluoride, on sodium fluoride, and its decomposition on moderate heating.[5] Sodium fluoborate, on the other hand, shows remarkable stability, as it can be melted and heated up to 900°C. without decomposition.[4] Sodium hydroxytrifluoborate, $NaBF_3OH$, has been prepared by evaporation or precipitation with ethanol from an aqueous solution of 2mols. of sodium hydrogen fluoride and 1mol. of boric acid.[141]

The double salt NaF,Na_2SO_4 is formed from aqueous solutions of sodium fluoride and sulphate,[86] while solutions of trisodium orthophosphate and sodium fluoride yield a double salt $NaF,2Na_3PO_4,19H_2O$.[142]

The need of the aluminium industry for synthetic cryolite has stimulated interest in complex formation between sodium and aluminium fluorides. Addition of sodium fluoride to a saturated solution of aluminium fluoride results in the precipitation of double salts, the composition of which appears to vary to some extent with the concentration of sodium fluoride in solution. It has been claimed that $3NaF,AlF_3$ appears only with higher concentrations of sodium fluoride, and that the more stable salt is $11NaF,4AlF_3$;[143] other workers find no indication of this compound but a series of solid solutions of $AlF_3,3H_2O$, $3NaF,2AlF_3$, and NaF.[144]

With beryllium fluoride, the compounds $NaBeF_4$, $NaBeF_3$, $Na_3Be_2F_7$ and Na_3BeF_5 have been formed from fused mixtures.[145] Na_3InF_6 has been prepared from aqueous solutions of indium fluoride, sodium fluoride and hydrofluoric acid.[146] From ferric fluoride solutions, $5NaF,2FeF_3$ is formed; this salt is almost insoluble in sodium fluoride solution.[147] A double chromium sodium fluoride, $3NaF,CrF_3$, is formed in a similar manner.[148] A number of double fluorides have been found with uranium, thorium and lanthanum.[149] Tungsten trioxide, fused with sodium fluoride in the absence of air, forms $Na_3WO_3F_3$, whereas in the presence of air oxygen is exchanged for fluorine, yielding Na_3WO_4F.[150]

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SECTION XXXI

SODIUM CHLORIDE

By F. HOLMES, J.M. THOMAS and J. P. JONES

OCCURRENCE

By F. HOLMES

Sodium chloride occurs very widely throughout the world. Indeed it would be as easy to list the materials in which it does not occur as to name those in which it may be found, at any rate in traces. The chief sources, however, and the only ones of commercial importance, are in extensive solid deposits and as a solution. The obvious instance of the latter is the ocean and other surface waters but underground brines may also be found.

Solution. Oceanic and Other Saline Waters.

The ocean shows remarkable constancy in the relative proportions of the most important ions present, although the absolute concentration may vary to some extent. The amounts of these ions have been given many times and are quoted in Mellor, II, 523. The figures cited by Svedrup, Johnson and Fleming[1] for a sea water containing about 35 parts per thousand of solid are given in Table I as a later example. Analyses given by Nisikawa, Okuno, Maeda and Ogato[2] for 125 samples taken between Yokohama and London and for 104 taken between Yokohama and San Francisco show good agreement with these figures.

TABLE I.- COMPOSITION OF SEA WATER

Ion	parts per 1000	% of total solids
Na^+	10·556	30·61
Mg^{2+}	1·272	3·69
Ca^{2+}	0·400	1·16
K^+	0·380	1·10
Sr^{2+}	0·013	0·04
Cl^-	18·980	55·04
SO_4^{2-}	2·649	7·68
HCO_3^-	0·140	0·41
Br^-	0·065	0·19
F^-	0·001	0·00
H_3BO_3	0·026	0·07
Total	34·482	99·99

Water must contain the dissolved inorganic solids largely as free ions, but the sodium and chloride ions are present in nearly equivalent amounts, so that the statements often made that sea water contains about 2·7% or 2·8% of sodium chloride, approximately 80% of the total solids, are understandable. Since it has been estimated that the total volume of the earth's hydrosphere is about 3×10^8 cubic miles a vast amount of sodium chloride is potentially available from it.

The analytical figures may be appreciably different for seas near land where rivers discharge; and of course the salinity of rivers and of land-locked water masses may be different again, subject as they are to influences such as periodic evaporation. Analyses for a number of different lakes are given in Mellor, II, 524. The analytical difference may be in composition as well as in total amount; in fact the solids obtained from some saline waters may be very different from those of sea water. It has been suggested that for convenience brines may be divided into three main types based on the predominant anion, the most important cations usually being sodium, magnesium, potassium and calcium. The first type has chloride as the main anion. Sea water and many terrestrial brines are of this type; sufficient chloride is present to be equivalent to all the sodium and to most of the next most plentiful element, magnesium. The second type, terrestrial brines with more sodium than chloride, are rare and they generally differ from sea water in having more calcium than magnesium together with a greater proportion of sulphate. The last type, the 'alkaline' or 'volcanic' brines, have an increased carbonate content, most containing carbonate, sulphate and bromide, with a smaller amount of chloride. There is of course an almost complete gradation between the types; but it is obvious that many naturally occurring 'brines' would not give large quantities of sodium chloride and cannot be looked upon as potential sources of it, although they are often utilized in the manufacture of other alkali or alkaline earth salts.

As examples of the variations the following may be quoted from the many hundreds in the literature:-

1. Texcoco Lake (Mexico).[3] Analysis of solid left on evaporation - NaCl, 50%; Na_2CO_3, 40%; KCl, 6%; $NaBO_2$, 2%; Na_2SO_4, 2%.

2. Didwana (India).[4] Total solids content, 23–30 parts per thousand containing - NaCl, 16–23; Na_2SO_4, 5–7·5; Na_2CO_3, 0·5; $NaHCO_3$, 0·5. Natural cooling of the brine in winter, when $Na_2SO_4 \cdot 10H_2O$ crystallizes, followed by solar evaporation in summer to give sodium chloride shows how simple means are often used to isolate substances from these rather complex mixtures.

3. Hocking Valley, Ohio.[5] Brine from a depth of about 2700–2800 ft. gave on analysis - Na^+, 17·69; K^+, 0·68; Ca^{2+}, 14·93; Mg^{2+}, 2·98; Cl^-, 63·04; Br^-, 0·55; SO_4^{2-}, 0·03; HCO_3^-, 0·04% of the solids.

4. Bay City, Michigan.[6] A Silurian brine gave the remarkable analysis of - Na^+, 0·02; K^+, 21·36; Ca^{2+}, 206·3; Mg^{2+}, 7·2; Cl^-, 403·2; Br , 3·50; HCO_3^-, 1·21 g. per litre. This is a total solids figure of 642·8 g. per litre.

5. Dzhaksy-Klych Lake (U.S.S.R.).[7] The brine contains - NaCl, 10·50%; KCl, 1·18%; $MgCl_2$, 9·92%; $MgSO_4$, 7·65%.

6. Lakes Deshsheshak and Bekesh-Sor on the northern delta of the River Volga.[8] A layer of solid crust on the surface, and samples of the brine, had the compositions given in Table II.

TABLE II.- COMPOSITION OF BRINES FROM LAKES IN THE VOLGA-DELTA

Component	Lake Deshsheshak brine		Lake Bekesh-Sor brine		Solid Crust
	July 1931	May 1932	July 1931	May 1932	
NaCl	6·73	24·02	12·27	23·29	93·10
KCl	0·11	0·03	0·24	0·10	-
$MgCl_2$	15·03	1·57	8·69	1·25	0·43
$CaSO_4$	<0·10	0·20	0·10	-	0·94
$MgSO_4$	7·17	1·05	8·65	1·29	0·23
$MgBr_2$	0·12	-	-	0·01	-
insoluble	-	-	-	-	1·26
water	-	-	-	-	4·20

7. Inder Lake, U.S.S.R.[9] The water contains - NaCl, 19·6–23·9; KCl, 0·10–2·1; $MgCl_2$, 1·74–4·57; $MgSO_4$, 0·35–0·49; $CaSO_4$, 0·04–0·3; $Ca(HCO_3)_2$, 0·05–0·13%.

8. Lake Ebeity, U.S.S.R.[10] The water contains - Na^+, 8·97; K^+, 0·017; Mg^{2+}, 0·57; Ca^{2+}, 0·022; Cl^-, 9·25; Br^-, 0·025; SO_4^{2-}, 8·46; HCO_3^-, 0·072%. In autumn and winter the lake bottom is covered with a 25–30 cm. layer of salts, of composition - halite, 3; mirabilite, 84·17; thenardite, 11·62; clay etc. 1·17%.

9. Thermal salt springs of Misasa, Japan.[11] Analysis - Na^+, 0·6210; K^+, 0·0653; Mg^{2+}, 0·0044; Ca^{2+}, 0·0534; Cl^-, 0·867; SO_4^{2-}, 0·1635; HCO_3^-, 0·1978 g. per litre.

Solid Sodium Chloride.

Rock salt or halite is the name given to naturally occurring solid sodium chloride, generally found in extensive underground deposits. Its purity varies but occasionally pure colourless crystals occur, their purity exceeding 99·9%; these are quite transparent and are a source of pure sodium chloride for such uses as in the prisms and lenses of infra-red spectrophotometers. Rock salt may also be coloured, generally in the yellow-brown-red portion of the spectrum, owing to small amounts of impurities. Occasionally the colour is blue or purple, but for this, as will be seen later, an explanation may be found in the nature of the crystal lattice rather than in any direct effect of impurities. The purity of halite varies from one deposit to another and with its location inside a particular deposit, and is usually highest near the middle of a vein. Most of the salt mined in the United States has a purity of more than 98%, in Great Britain of over 95%. The reported composition from a number of localities is given in Table III,[12,13] the values being similar to the much older figures previously quoted. (Mellor,II,524).

TABLE III.- COMPOSITION OF ROCK SALT

	Cheshire, England 12	Mayo Salt Mine, India 12	Stassfurt, Germany 12	Malagash, Nova Scotia 12	Mohei, Yunnan, China 13	Cotinguiba, Sergipe, Brazil 14	Swakopmund, S.W. Africa 15*	Iletsk, U.S.S.R. 16
NaCl	95·60	98·86	97·53	99·09	97·37	99·40	98·42	93·62–99
KCl	-	-	-	-	0·12	trace	nil	-
$MgCl_2$	0·08	nil	-	0·03	0·07	-	-	0·00–0·05 (inc. $MgSO_4$)
$CaCl_2$	0·03	-	-	0·12	0·90	-	0·24	-
Na_2SO_4	-	0·57	0·43	-	-	-	-	0·00–0·03
$CaSO_4$	1·29	-	1·29	0·40	1·13	0·30	0·54	0·72–1·09
$MgSO_4$	-	-	0·23	-	-	0·07	-	
insoluble	3·00	-	-	0·36	0·02	0·12	0·46	0·16–0·50

The examples given are all for deposits of fairly pure sodium chloride, but the evaporation of many brines will yield saline deposits containing a large proportion of other salts. Again, if sea water is gradually evaporated, layers of precipitated salts will be formed as the solubility of different phases is exceeded. In the Ozinky region of the U.S.S.R., for example,[17] deposits at a depth of about 1200 ft. are 70–90% kieserite; at shallower depths carnallite, and still nearer the surface are polyhalite. Thus saline deposits may sometimes be used for the recovery of potassium or magnesium salts rather than for the production of sodium chloride. A recent review[18] deals at some length with stratification in the light of the complicated phase systems involved during the evaporation of oceanic water.

Rock salt may occur in either of two ways. The first is as strata or 'lenses', presumably as originally deposited. Such a deposit may not be actually continuous throughout its extent since, even if not interrupted subsequently, it must conform to the shape of the surface on which it was originally deposited. These strata are often very large in total area. It has been estimated, for example, that two of the largest in the United States - the Salina formation of the Northeastern States, and the bed mined in the Southern States - occupy about 70,000 and 100,000 square miles respectively. But probably the most extensive deposit in the United States is the Louann beds at a depth of about 10,000 ft.; it has been suggested that this may cover about 180,000 square miles. The second mode of occurrence is as disrupted domes, ridges or bosses, much smaller in extent and often near or at surface level. These also occur quite widely.

Origin of Rock Salt.

In the original Treatise (Mellor,II,524) it was suggested that nearly all deposits of solid sodium chloride are marine in origin, and this suggestion has been implicit in the present discussion. The alternative hypothesis of volcanic origin seems now largely discredited except,perhaps,in a few special cases. Almost all modern speculation assumes that the deposits were formed by evaporation under desert conditions, or at least by evaporation at a rate faster than the replenishment; this evaporation might be periodic. None of the proposals is satisfactory in all cases however, and many papers[19-34] discuss the geological conditions in which salt is found. Vertical displacement of the strata is supposed to have given rise to salt domes, the salt being first buried under newer rocks and then flowing upward through cracks or faults, the flow being made possible by great pressure causing the salt to become plastic. On this subject also there is a considerable volume of literature.[35-51]

General.

Many other analyses of brines and of salt deposits have been reported, the papers being so diversified in content that it would be impossible to summarize them adequately. A large number are of Russian origin.[52-82] Some of these are of particular interest because of the extreme variation between summer and winter temperatures; this leads to stratified deposits that have often been investigated with the brines. Attempts have been made, particularly in the more recent papers, to relate the findings to the geological history of the area. Mention may also be made of a series of articles on the evaporites of northeastern England.[83-86] Others range from the analysis of a 'salt lick' in Southern India[87] ($NaCl$, 7·1%; Na_2SO_4, 4·6%); to that of the salts from the fumaroles on the crater of Mount Vesuvius[88] ($NaCl$, 79·5%), where the salt is presumably derived from the hydrogen chloride in the volcanic gases and is not of marine origin. The variation in salt content of the river Rhine[89] and of the Raselm[90] seas have been discussed and are examples of changes in our own time. The fourfold increase in chloride content of the Rhine in 1936–44 compared with 1907–21 was attributed to wastes from the Upper Rhine salt mines.

General summaries of sodium chloride occurrence have been given for many areas of the world, often in conjunction with reports on other mineral deposits of economic importance. Those which have appeared since the publication of the original Treatise include information concerning the Argentine[91-93] (and the province of Cordoba[94]), Austria (Bad Ischal[95]), South Australia,[96] the Belgian Congo (Lake Albert-Edward depression),[97] Canada[98] (and Nova Scotia,[99,100] British Columbia,[101] Alberta,[102,103] Manitoba[104]), Chile,[105] China[106] (and Szechuan Province[107,108]), Columbia,[109] Ethiopia,[110] Southwest France,[111,112] French Morocco,[113] Germany (North Hanover,[114] Heilbronn[115]), Gold Coast (Voltaian Basin[116]), Greece (plains of Salonika[117,118]), India (Gulbarga District of Hyderabad,[119] Mandi state,[120] Sambhar Lake[121]), Italy (Sicily[122]), Mexico[123] (Valley of Mexico,[124] Michoacan[125]), Palestine,[126] Tanganyika Territory,[127] Tibet and China,[128] Turkey (Cayi Region[129]), Uganda,[130] U.S.A. (South-Central,[131] Ohio,[132] Oklahoma,[133] Pennsylvania,[134] West Virginia[135-137]), U.S.S.R.(North European U.S.S.R.,[138] South Urals,[139] Kamysh-Kurgansk region,[140] North Caspian region.[141] Sham-Shikal deposits[142]).

Other Modes of Occurrence.

As has been stated previously, sodium chloride is not only to be found in brines and solid deposits. Its presence has been investigated in rain, snow, fog and other climatic phenomena as well as in most animate and inanimate objects, and it has been found in amounts varying from traces to considerable quantities. In Mellor, Supplement II part I, p. 264 the occurrence of chlorine is discussed; doubtless in many of the cases mentioned it occurs as sodium chloride.

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PRODUCTION OF SODIUM CHLORIDE

By F. HOLMES

In Mellor,II,525-526, very brief accounts are given of the mining of rock-salt, and of the evaporation of brine - either naturally occurring or made from rock salt - to give salt. These are still the methods used throughout the world. Conditions of manufacture have however changed so much that a considerably longer account is desirable.

Mining of Rock Salt.

Sodium chloride may be obtained from solid rock salt deposits either by mining or by pumping down water, dissolving the rock salt and pumping it up again as brine. Mining it as a solid gives a cheap, though obviously impure, salt and a great amount is produced in this way. The mining methods employed are fairly standard. Shafts are sunk and the salt is mined in much the same way as coal - in fact coal cutting machinery and coal mining explosives are often used. Sections of the salt face are first undercut and overcut and then removed by blasting. The lumps of salt are mechanically picked up and transported to the surface. The mines are generally cool and often have natural ventilation.

The salt so obtained is usually not purified but simply crushed, screened and sold according to grading. Imperial Chemical Industries Ltd., from the Meadow Bank salt mine in Cheshire, market the following grades:

Lumps.
Grade 4 Ground Rock Salt (screened through $\frac{1}{4}$ in. mesh).
Grade 5 Ground Rock Salt (ground and pulverized).

The International Salt Company, from the Retsof mine, have four commercial sizes:

No. 2. (Through $\frac{3}{4}$ in. sieve, retained on No. 4 sieve).
No. 1. (Through $\frac{3}{8}$ in. sieve, retained on No. 8 sieve).
Coarse C. (Through $\frac{3}{8}$ in. sieve, retained on No. 12 sieve).
Fine C. (Through No. 8 sieve).

Descriptions have been given of the operation of the mines and of the processes involved.[1-3] The purity of the salt so marketed is of course that of the rock salt, *i.e.* between 95% and 99% for most of the sources extensively worked, although lower in some countries. That from the I.C.I. mine, the only one now worked in Britain, is 95%; that from most American mines about 98.5%. The residue is other alkali and alkaline earth salts and, particularly with the British material, some earthy matter. The salt produced by mining is generally coloured; it is used for such purposes as ice clearance and for livestock.

Occasionally, though not usually where modern works exist, the rock salt is purified. This is generally done by dissolving it in water and preparing pure sodium chloride from the brine using ordinary modern practice to be described later, although even a straight recrystallization will remove insoluble matter and some of the soluble impurity.[4,5] Other methods of purifying rock salt have been suggested, such as melting the impure salt[6-8] or dissolving it in liquid ammonia.[9,10]

Salt from Brine

Pure salt is generally made by evaporation of brine. This brine may be sea water or it may be obtained by pumping water down to rock salt beds. Little is obtained from other brines. Although these may in some places be important local sources the total amount obtained from them is comparatively small; often it is incidental to the production of other useful salts such as potassium chloride, sodium carbonate, sodium sulphate or borax. An instance of this is Searles Lake in California.[11]

Of the two more usual sources the formation of brine underground is the most widely used. A point here is that the brine so formed is almost saturated whereas that from the sea must undergo preliminary concentration. As will be seen this preliminary evaporation is no disadvantage when solar heat can be utilized, but there are numerous references to processes in which heat is applied in more orthodox ways[12-18] to evaporate sea water at high temperature and pressure. In three such processes several of the constituent salts are worked up.[16-18]

Whatever the source of brine and of heat the principle involved is evaporation until the major part of the sodium chloride has been crystallized from solution. At the same time other components of the brine will be precipitated and the salt will not be pure.

Open Pan and Grainer Salt.

The simplest procedure is to heat the brine from below in shallow open vessels - the so called 'Open-Pan' method. This has been used in Britain since Roman times, the original lead pans being replaced by iron pans in medieval times. Such rather primitive methods are still used in many parts of the world; processes used in China[19] and Japan,[20] for example, use coal for heating and give an impure product. In modern works the tanks are generally welded mild steel[21] and may be up to 140 ft. long and 25 ft. wide. Concrete[22] has been suggested as a possible material. Brine is fed in continuously and the salt which crystallizes is raked to the side, whence it is periodically removed. A scale of calcium salts gradually forms on the bottom and must be removed since it is a poor conductor of heat. The type of salt produced by this process depends on the temperature at which evaporation takes place and the time which elapses before the solid salt is removed from the vessel. If fine salt is desired the temperature is kept near the boiling point of the brine and the solid may be cleared daily. If a very coarse salt is needed then a much lower temperature is used and the salt may stay in the bath for a week.

In good modern practice the pan is heated by a series of steam coils in the vessel and near to the bottom. The salt so obtained is called 'Grainer Salt'. This type of heating is common in the United States, Canada and Germany, but not in Great Britain. The crystal form is controlled by the amount of steam passing through the coils. The general aim is to obtain large crystals, and to help achieve this the solution is not stirred or disturbed. As evaporation proceeds salt crystals are formed at the surface and grow there, held by surface tension. As they continue to overgrow they gradually sink to the bottom, growing on top in the form of hollow pyramids, 'hopper crystals', so-called by reason of their shape. These eventually break and sink to the bottom where they are periodically removed by hydraulically controlled rakes. It is possible to use such rakes, as the lack of bottom heating keeps the base level. The salt is removed and is washed, dried and graded. Calcium salts, if not removed from the brine, tend to cake on the steam pipe, as they did on the bottom in the old open-pan method.

Vacuum Salt.

The second method of removing water from brine is by heating under vacuum. Vacuum evaporation has been standard engineering practice for very many years and the first large plant in Great Britain using this principle for the production of salt was opened at Winsford in 1905. A vacuum unit consists of a cylindrical vessel, generally with a conical top and bottom, having in the central portion a steam heating unit or 'calandria'. If one unit is operated by itself, low pressure waste steam or other heating gas circulates through the calandria, while brine enters at the bottom of the unit and reaches above the heating system. The brine boils and salt is deposited, gradually flowing out through the bottom against the current of incoming brine, and subsequently being filtered and dried. The steam given off by evaporation is condensed and a partial vacuum is formed in the system. Most works however have three or four units in series, each perhaps 20 ft. in diameter and twice that height. Fresh concentrated brine enters the bottom of each unit, but they are run as a 'multiple effect' evaporator, the first unit being heated by waste steam, the second by steam given off in the first, and the third by steam from the second. Condensation of the steam during this evaporation causes each unit to be under lower pressure than the previous one. In this way a considerable saving of fuel is possible compared with open-pan or grainer methods. The salt sludge from the bottom of the units is filtered in a rotary vacuum filter and the brine returned to the evaporators. The filtered salt contains several per cent of moisture and may be stored in this state since there is a considerable market for undried salt. Generally, however, it is dried, in either a rotary or a vibratory drier heated by a countercurrent of air.

One advantage of the vacuum method is the lower fuel costs. Another is that it may be so easily made a continuous process. However, until very recently it could produce only a fine grained salt, and there is a considerable demand for the coarser 'grainer' salt, since many uses of salt require the particular specific surface of this product and of the so-called 'flake' grain - the fragments from the side of the hopper. So both processes often exist together in the same works and a patent describes how the steam may then be used to the best advantage.[23] The vacuum method, like the others, can suffer from calcium salts appearing as an impurity in the salt produced and as a deposit on the steam pipes. The former difficulty can be minimized since the incoming brine washes the outgoing salt; if the calcium salts (sulphate) are in very small crystals they are partially removed.

It has, however, now become accepted practice in both methods to purify the brine before crystallization. Several processes have been tried for this purpose but that most commonly used is the lime and soda process, or some variant of it, in which the brine is treated with a mixture of milk of lime and soda ash, the magnesium and calcium being precipitated as the hydroxide and carbonate respectively. In a Japanese patent[24] the calcium hydroxide is followed by magnesium oxide, hydroxide or carbonate, and by passage of carbon dioxide. A German patent[25] uses caustic alkali and an aged gelatinous precipitate, as for example basic magnesium carbonate from a previous batch. Barium carbonate has been suggested[26] but is expensive. It has been suggested[27,28] that removal of magnesium as hydroxide by means of sodium or calcium hydroxide may give a colloidal suspension at times, and that addition of starch, dextrin or gelatin aids the precipitation; addition of calcium carbonate helps. An earlier discussion of the problem[29] stated that colloid formation could be avoided by gentle stirring and a temperature of about 25°. A general discussion on the method itself may be mentioned,[30] together with a few of the many earlier patents that exist.[31-34] Other types of purification such as electrolysis[35] have been suggested but not generally accepted. A novel method[36] which is limited to batch processing consists of pumping brine at 200° and 15·86 atmospheres into an autoclave containing a molten cadmium-tin alloy (50/50) at 200°. A fluffy calcium sulphate deposits on the top of the melt and is later removed by filtration.

Purification of the final product is not now necessary in many modern plants but may be done in older ones. A normal purification is by washing with brine,[37] which will wash out fairly small amounts of soluble impurities. Melting has been suggested[38] but is not normally used. Chemical methods[39] are suitable only for fairly small batches. Treatment with ammonium alum[40] was said to give an 80% yield. It has been stated[41] that preliminary purification of brine with sodium carbonate for the vacuum method leads to 0·2–4·0% of sodium sulphate in the product, but that brine washing reduces this to 0·01–0·05% if crude brine is used, and to 0·06–0·10% with pure brine.

Attention has been paid, in recent years, to the crystalline form of manufactured salt. In grainer plants this is to gain efficiency; thus Gilkey and Shuman[42] have found that adding a surface-active material such as polyoxyethylenesorbitan monolaurate to the brine at less than 500 p.p.m. increased the rate of formation of hopper type crystals. In vacuum plants the object has been to produce a coarse grainer-like salt, so that both types may be produced by the very convenient vacuum process. Imperial Chemical Industries[43] have produced coarse grained salt by adding to a pure brine about 1 p.p.m. of a quaternary ammonium compound such as hexadecyltrimethylammonium bromide or a polyethenoxy compound, before evaporation. The same firm obtains low bulk dendritic crystals[44] with several spiky branches on each crystal. These are produced by vacuum evaporation of calcium- and magnesium-free brine containing a few p.p.m. of a modifying agent. Modifying agents are either, (*a*) compounds of formula $A(MX_6)$, such as $K_3[Fe(C_2O_4)_3]$ or $K_4[Fe(CN)_6]$, (*b*) water-soluble salts of carboxylic acids having no more than twenty carbon atoms, (*c*) a variety of other inorganic and organic compounds. A Swiss modification[45] to obtain coarse vacuum salt is to use a propeller in the unit.

General.

A number of processes have been described in some detail. The Morton Salt Company[46] at its refinery in Texas, U.S.A. produces both rock salt by mining, and brine by pumping from the strata. The rock salt is sold as both coarse and fine sorts, and in twelve grades. The brine is purified and evaporated by either vacuum or grainer techniques. The grainers work at an average temperature of 215°F. and the pans are lined with neoprene rubber. In the whole plant much use is made of modern new materials such as stainless steel, monel metal, and steel coated with a phenolic resin. A similar, earlier, review[47] was published about the Goderich Salt Company, Ontario. The novel process operated by the International Salt Company has been described[48] in some detail. Impure salt is fed into circulating brine. This is then heated by steam, and diluted by condensed steam when salt dissolves. After the insoluble material has settled the nearly boiling brine is fed into a flash crystallizer working at a lower temperature. Here the brine cools and liberates about the same amount of vapour as it originally gained so that about the same amount of salt is crystallized as was dissolved in the earlier stage. This salt is filtered or centrifuged and the process is continuous. A particular point is that calcium sulphate becomes decreasingly soluble in brine as the temperature is raised above 180° F., so that on cooling to 180° or less in the flash crystallizer no calcium sulphate is precipitated with the sodium chloride. The brine, with its pH maintained at about 10.8 by caustic soda, produces salt which when washed quickly, or when rewashed with brine, has the analyses given in Table IV.

TABLE IV.- ANALYSIS OF SALT

	quickly washed salt	re-washed salt
Moisture	0.020	0.020
$CaSO_4$	<0.005	0.001
$CaCl_2$	0.002	0.0005
$MgCl_2$	<0.001	0.0002
Fe_2O_3	0.000	0.0000
NaCl (dry basis)	99.992	99.998

A fairly comprehensive review[49] discusses improvements in engineering as applied to salt production, together with diagrams and flow sheets. In the second article the Alberger, Morton and International Company's methods are discussed in some detail. The advantages and disadvantages of the Richards (Multiple Effect) Process are considered, together with the uses and difficulties of both the grainer and vacuum processes.

Another very detailed description of both the grainer and vacuum-pan methods of production has been given by Hester and Diamond,[50] and one of the uses of triple-effect forced circulation evaporators by Simmons.[51] For the drying of salt after its production a fluidized crystal drier has been described[52] which effects a saving in fuel and has general working advantages. Shorter reviews have also been published of process control in the salt industry,[53] and of evaporation installations,[54] the latter specifically for 1951.

Consideration has naturally been given to the dissolving of rock salt in the strata and the removal of the brine so formed. Various piping systems have been designed and are discussed in the literature.[55-57] Examples using the technique are given for Holland[58,59] (together with the subsequent treatment of the brine), for some of the Alpine deposits[60] which cannot be mined because of the involved stratification, and for Natrium, West Virginia,[61] where mining is difficult because of the depth of the deposits and the high temperature and drilling is difficult because of roofs caving in after a dome has partly dissolved.

Solar Evaporation.

In many parts of the world with a hot and fairly dry climate salt is produced on the coast by the simple method of solar evaporation. In principle this consists of taking a piece of flat ground just below high tide level and building a wall round it. A channel is cut from the sea to the pond thus formed, so that water flows in at high tide to replace that lost by evaporation. Salt gradually accumulates in the lagoon and is removed. Aden, Portugal, Spain, France, Corsica, Italy, Cyprus, Turkey, China, California, Formosa and India all produce salt by this method. Under primitive conditions the process may be as simple as that given above, but generally it has been improved, and in the most modern works may be run on the most rigid scientific and engineering principles. The rather crude yellowish deliquescent salt obtained by the simplest techniques may be purified somewhat by washing, but salt from a modern works is reasonably pure.

The most usual improvement on the empirical method is to have a series of small interconnected ponds or lagoons, the brine being allowed to proceed from one to the next as it becomes more concentrated. Finally the sodium chloride crystallizes. In this way constant dilution of the crystallizing solution is avoided. Also, since the different constituents of sea water have different solubilities a purer salt is obtained.

Most of the solar salt produced in the United States comes from the Californian coast. Descriptions have been published, in 1937[62] and 1952,[63] of the operation of one of the large works in this area and a resume will serve to illustrate the working of an efficient modern solar evaporation system. The following description relates to the works near San Francisco of the Leslie Salt Company, claimed to be the largest in the world. Concentrating ponds and crystallizing ponds are arranged with four feet high walls on ground low enough to be filled through floodgates without pumping at high tide. Nine or ten concentrating ponds and several crystallizing ponds form a single production unit. The concentrating ponds may have random shape but the crystallizing ponds must be regular in form. The concentrating ponds have about fifteen times the surface area of the crystallizing ponds. New ponds need time to become impervious - about five to seven years is the ordinary time to reach maturity - after which up to forty tons of salt per acre per year may be achieved in this particular plant.

The first concentrating pond is flooded in the autumn after evaporation has increased the concentration of dissolved salts in the water of San Francisco Bay to about 3·5%. As evaporation proceeds and the density increases, the brine is gradually moved forward through the series of evaporating ponds, gravity and wind being used as far as is possible. When the density has reached 24·6–26·0° Bé. the solution is allowed to enter the crystallizing lagoons, remaining there until the density is 29·0° Bé. Between these limits the maximum quantity of high purity sodium chloride separates. The significance of the upper and lower densities is that below 25° Bé. most of the gypsum crystallizes out, and the speed of movement is slow enough for this to have settled before the brine enters the crystallizing ponds. At the same time carbonates of iron, magnesium and calcium come out. At 30° Bé. significant quantities of magnesium salts begin to crystallize. The liquid removed from the lagoons at about 30° Bé. is rejected although it still contains significant quantities of sodium chloride; it is often used for the recovery of bromine and magnesium. The composition at 28° Bé. is given as NaCl, 16%; $MgCl_2$, 6%; $MgSO_4$, 4·2%; KCl, 1·4%; Br^-, 0·1%. At 30° Bé it is NaCl, 12·5%; $MgCl_2$, 8·7%; $MgSO_4$, 6·1%; KCl, 1·9%; Br^-, 0·2%. In this works in 1952 there were about 29,000 acres of brine ponds, yielding up to 900,000 tons of salt a year. According to the earlier paper salt cakes about four to six inches thick are obtained in a season, and this salt is washed to remove clay, when it has a purity of more than 99·9%. The calcium sulphate precipitated during evaporation helps to make the concentrating lagoons impervious. These are of clay rather than concrete since not only is clay cheaper but crystallization is better promoted by it. A layer of algae on the bottom facilitates the recovery of the salt.

Details have been published of processes in other countries, in which similar principles are adopted. Móscu[64] has suggested details for such a process in the Argentine, and gives figures for the composition of evaporated sea water at densities of 3·5° Bé. (the original water), 25°, 30° and 35° Bé. Similar figures have been given by Maeda.[65] Chorower[66,67] has discussed in some detail the effect of a number of factors on the evaporation of brine. In particular climatic conditions such as atmospheric temperature, humidity and pressure, and wind condition, were studied. Kane and Kulkarni[68] have discovered that the solar evaporation of brine can be accelerated by about 10–20% on addition of very small amounts of Naphthol Green B.

Several reviews of solar salt industries have appeared. These include:-

(1) The Phillipines[69] where the Californian method previously outlined has been shown to give a much better product that the older methods.

(2) Australia,[70,71] where solar evaporation is of great importance, particularly in South Australia and the Eastern States.

(3) The Bulgarian Black Sea coasts,[72] where, in 1946, almost 100,000 tons was produced, and purified by washing.

(4) South Africa.[73] The deposits are all as 'pans' in flat dry country.

(5) Lake Texcoco (Mexico).[74] This lake, as was said earlier, gives on evaporation a solid containing about 50% of sodium chloride and 40% sodium carbonate.

A short review[75] appeared in 1937 giving the manufacturing processes and characteristics of solar salt at that date.

Freezing of Brine.

If sea water is partially frozen the ice formed is practically pure water and repetition of this process leads to a much more concentrated brine. There are no indications that this has been applied to the large scale production of solid sodium chloride although it would be theoretically feasible in cold countries. It has, however, been utilized for the production of solid concentrated brine. Frozen eutectic sodium chloride has been made[76] by freezing a 23·3% aqueous solution of sodium chloride, and the ice produced is flaked. The product melts at −21·1° and absorbs 101·5 B.t.u. of heat per pound of ice and has been said to be commercially available. The formation of different phases as sea water is concentrated by freezing has been studied by Nelson and Thompson.[77] After about 80% of the water has solidified $Na_2SO_4,10H_2O$ begins to crystallize at −8·2°, the sulphate concentration in the brine falling markedly. At −22·9° $NaCl,2H_2O$ is precipitated in large amounts; the amount of brine has now fallen to about 2% of the original. Sodium chloride continues to precipitate with further fall in temperature, until at −36·0° KCl and $MgCl_2,12H_2O$ begin to appear but not in the form of carnallite. It is suggested that at −54°, slightly above the point at which the residual brine solidifies, $CaCl_2,10H_2O$ begins to precipitate.

A Swedish patent[78] has also been filed to recover the various salts from sea water, and a Japanese patent[79] to recover the salts from the sea water residues left after the production of sodium chloride. Both use a combination of freezing and chemical treatment.

General.

Many reviews relate to the winning of sodium chloride in general, and its production in various parts of the world. The value of these varies considerably and the older ones do not always represent the situation at the present time. Among those devoted to the Americas may be mentioned Brazil[80] (1929), Great Salt Lake[81] (1932), Louisiana and Texas[82] (1935), Southern States of the United States[83] (1940), Mexico[84] (1942), Peru[85] (1944), Ohio[86] (1945), the Pacific coast[87] (1947) and Louisiana[88] (1953). Those from other areas may be exemplified by India[89–91] (1924, 1952, 1953), Germany[92,93] (1937, 1943), Poland[94] (1925), Portugal[95] (1934), the Aegean Sea[96] (1943), Victoria, Australia[97] (1949). Among more general reviews there are production[98,99] (1935, 1936), mining[100] (1942), production and uses[101] (1941), marketing[102] (1939).

Two annual reviews of production and trade are of the greatest use. The first is the section on 'Salt' in the Review of the Mineral Industries, contained in the United States 'Bureau of Mines Minerals Yearbook'. The second is to be found in the annual section on 'sodium salts' in 'Mineral Industry'.

Production of Salt

World production of salt in the past few years is estimated each year in the Minerals Yearbook of the United States Bureau of Mines. The figures quoted in the Yearbook for 1957[103] are reproduced in Table V.

The most important producers in each continent in 1957 (figures taken from the same source[103]) are given in Table VI.

TABLE V - WORLD PRODUCTION OF SALT (short tons)

	Average 1948–52	1953	1954	1955	1956	1957
N. America	18,982,000	22,382,000	22,298,000	24,523,000	26,520,000	26,393,000
S. America	1,813,000	1,792,000	1,842,000	1,780,000	1,750,000	1,911,000
Europe	23,600,000	27,100,000	28,200,000	28,200,000	29,800,000	29,900,000
Asia	9,553,000	12,300,000	12,700,000	13,900,000	13,800,000	17,100,000
Africa	1,472,000	1,500,000	1,660,000	1,540,000	1,675,000	1,640,000
Oceania	302,513	347,000	427,130	416,760	470,268	449,468
World total (estimated)	55,700,000	65,400,000	67,100,000	70,400,000	74,000,000	77,400,000

TABLE VI.- SALT PRODUCTION IN THE CHIEF PRODUCING COUNTRIES IN 1957

		Production (short tons)
N. America	United States	5,341,586 (rock salt) 18,512,433 (other salt)
	Canada	1,771,800
	Mexico	265,000
	Bahamas	191,339
S. America	Brazil	826,700
	Argentine	465,726
	Columbia	228,223 (rock salt) 86,862 (other salt)
Europe	U.S.S.R.	7,200,000
	Great Britain	5,479,057 (other salt) 98,710 (rock salt)
	Germany (West)	3,597,940 (rock salt) 357,148 (other salt)
	France	3,586,000
	Germany (East)	1,874,000
	Italy	1,641,421
	Poland	964,521 (other salt) 440,924 (rock salt)
	Spain	881,848 (other salt) 558,302 (rock salt)
Asia	China	8,820,000
	India	4,040,967 (other salt) 4,856 (rock salt)
	Japan	917,169
	Turkey	493,681 (other salt) 10,075 (rock salt)
	Taiwan	426,696

continued on following page

TABLE VI.- continued

		Production (short tons)
Asia	Korea	406,962
	Pakistan	220,462 (other salt) 174,349 (rock salt)
Africa	Egypt	550,000
	Eritrea	220,460
	Union of S. Africa	160,743
	Tunisia	143,300
	Algeria	110,000
Oceania	Australia	440,900

In the United States itself the salt sold or used by producers in 1957 is given in Table VII.

TABLE VII.- SALT PRODUCTION IN THE U.S.A. 1957[103]

Method of production	short tons
Evaporated:	
Open pan or grainer	399,806
Vacuum pan	2,158,627
Solar	1,146,024
Rock Salt:	5,341,586
Sold as brine:	14,518,744
Total	23,854,019

Of this total, eight plants each produced more than one million tons, six produced between half a million and one million tons each, thirty between one hundred thousand and half a million and twenty six of the rest less than ten thousand tons each.

It will be noted from the figures given in Table VII that 60% of the salt used in the United States in 1957 was supplied as brine. For many industries this is satisfactory since the solid is not required. In many cases, however, the brine must be very pure; if a source of pure natural sodium chloride is not available manufactured pure sodium chloride has to be dissolved. Recently it has been suggested[104] that rock salt containing calcium sulphate can be made to yield brines of high quality by adding polyphosphates to the dissolving water, so eliminating the need for further purification in many industries. A German patent[105] for the purification adds alkali in the presence of alumina, followed by filtration.

Many instances are known of sodium chloride being recovered from manufacturing processes. Methods exist for its recovery from oil-well water,[106] and from waste liquors of soda factories[107] and tannery plants.[108] The amounts obtained however make no serious contribution to stocks and so need not be discussed further.

USES OF SODIUM CHLORIDE

Sodium chloride is used very widely in chemical industry as well as in the food industries and in various preserving processes.

Industrial Uses.

By far the largest amounts of sodium chloride are used in the manufacture of chlorine and of soda ash. In the United States in 1957 these two consumers took nearly 65% out of the 70% used by chemical industry. The other 35% was used in so many ways that it would be impossible to list them all. As an indication, Table VIII gives a breakdown of United States consumption in 1951, only the principal items being listed.

TABLE VIII.- CONSUMPTION OF SALT IN VARIOUS INDUSTRIES IN 1931 (short tons)[109]

Use	Consumption
Chlorine etc. production	4,709,000
Soda ash production	8,303,000
Other chemicals	835,000
Meat processing	747,000
Tanning	232,000
Canning and preserving	202,000
Other food processing	231,000
Refrigeration	192,000
Dyes and organic chemicals	129,000
Textile processing	124,000

These proportions change with time and place. By 1957 in the United States, for example, the amount used for chlorine manufacture was greater than that for soda ash.

The quality of the sodium chloride needed varies from one process to another and some countries have laid down specifications. S.S.A. No. 12–1943 of the South African Standards Institution indicates the position and part is given in Table IX.

TABLE IX.- SOUTH AFRICAN SALT SPECIFICATIONS(%)[110]

Constituent	Industrial Salt				Preservative salt		
	Super	No. 1	No. 2	No. 3	Meat packing	Fishery	Hide curing
NaCl (min.)	99·0	98·5	97·0	95·0	98·5	97·5	95·0
Ca (max.)	0·2	0·3	0·4	0·65	0·15	0·1	not specified
Mg (max.)			0·3	0·55	0·15	0·1	not specified
SO_4 (max.)	0·5	1·0	2·1	3·5	0·1	not specified	not specified
Insol. H_2O (max.)	0·05	0·1	0·1	0·15	0·1	0·1	0·15
Fe (max.)	-	-	-	-	-	-	20 p.p.m.

Table salt is identical with 'Super' quality and must in addition conform with trace element maxima; it must also pass through a B.S. 20 mesh sieve. Free running salt may contain up to 1% of calcium phosphate, magnesium carbonate, talc or starch.

United States Specification SS–S–31d of 1951 gives the specification for 'fine ground rock or evaporated table salt' and 'free running evaporated salt'. The first must be high quality crystalline salt and contain 'driers' - basic magnesium carbonate, or calcium carbonate or calcium phosphate - not exceeding 1%. Hydrated calcium silicate may also now be used. The granules must pass through a U.S. standard No. 16 sieve and not more than 10% through a No. 70 sieve. There must be less than 1·4% calcium sulphate, 0·5% calcium and magnesium chlorides and 0·1% insoluble matter (not including calcium sulphate or drier) calculated on a dry basis. Free running salt must meet an identical specification but the sieving requirements are different.

The British Standard Specification for Dairy Salt [B.S.S. 998, 1941] demands salt of purity greater than 99·7%, moisture less than 0·2% (dried salt) or 4% (undried salt), alkali (as sodium carbonate) less than 0·03% on a dry basis, insoluble not more than 0·03%, and maxima of sulphate (as sodium sulphate) 0·1%, calcium and magnesium 0·01%, iron 20 p.p.m., copper 2 p.p.m., arsenic 1 p.p.m. and lead 5 p.p.m.

Table Salt.

Salt for domestic purposes as often produced has tended to become sticky or to cake. This behaviour is caused by the hygroscopic impurities such as calcium and magnesium chlorides. Changing humidity of the air may lead to alternate deliquescing and drying of the salt surface, resulting in the growing together of the crystals and the loss of free flowing properties. This has been overcome by the addition of a stabilizer, which either forms non-hygroscopic compounds with the impurities or forms insoluble substances which cover the surface of the crystals and prevent the access of moisture. Many substances have been suggested for the purpose. The most important are carbonates, usually of sodium[111,112] calcium[114,115] or magnesium,[113] or phosphates,[116-119] usually of calcium. Magnesium oxide,[120] sorbitol,[121] glycerol[122] and calcium lactate[123] have also been mentioned. More recently magnesium stearate[124] and magnesium and calcium silicates[125] have been advocated.

It has been usual to allow iodide as a trace element in table salt, since it is a prophylactic against goitre, and in fact iodides are often added for this purpose. Generally there are statutary requirements as to amount. In Great Britain the upper limit is 1:50,000, in the United States and Canada it is 1:10,000 and in Germany 1:100,000. A number of workers have called attention to the possibility of loss of iodine.[126-128] Under some conditions this may be considerable, as when the salt is used in the preparation of food.

Pure Sodium Chloride

Modern vacuum salt contains only small amounts of impurities but attempts have been made to prepare very pure sodium chloride from less pure materials. Goto[129] has patented a process for purifying very crude salt for medicinal purposes by calcining, mixing with aqueous sodium carbonate and evaporating to dryness, then extracting with ethanol. Other attempts have been made using the dihydrate. Thus Nikolaev and Stepanov[130] showed that a recrystallization at −7° to −8° increased the purity of a rather impure Russian salt from 96·4% to 97·7%. A second recrystallization brought it up to 98·9%. Nikolaev and Arnol'd,[131] after two recrystallizations of crude material under specified conditions at 3° to 4°, obtained salt with a purity of 99·99%, while a third recrystallization improved this figure still further. Meites[132] has given directions for a simple preparation, on a laboratory scale, of sodium chloride sufficiently pure to be used as a primary standard in titrimetry.

Books and Historical Reviews

Baas-Becking[133] and Freydank[134] have contributed general accounts of the history of salt production. Other articles have discussed production in Germany,[135] Merseyside (Great Britain),[136] New York State,[137] Syracuse (U.S.A.),[138] Delaware (U.S.A.)[139] and China.[140] Books, largely on production and uses, have been written by Calvert,[141] Pecheux,[142] Altimir Bolva,[143] Stocker,[144] Max Schmid[145] and Zedlitz.[146]

Desalinification

In connection with its winning, the removal of sodium chloride from commodities, such as water, in which it is unwanted deserves some attention. Water which needs this treatment may be for human or agricultural use, or it may be for industrial purposes such as boiler feed water. The water concerned is generally brackish but it may even be sea water. The problem is not so much merely to purify the water but to do so as economically as possible. Experiments had been reported for some years before 1953 when a working party of O.E.C.C. studied the problem;[147] they considered ion exchange, freezing, electrodialysis and vapour-compression distillation. The process on which much interest has since centred is electrodialysis, made possible by the development of membranes having selective permeability for anions and cations. More recent summaries of work on the subject are by Neville Jones[148] and by Leicester.[149] Solar distillation has been the subject of experiment in Australia, and the results, including yield and efficiency, have been summarized by Wilson.[150] Wilson suggested that batch operation was most efficient, the overall efficiency at noon being 62–69%, and the overall daily efficiency about 50%, while average daily yields (lbs./sq.ft./day) varied from 0·79 to 1·46 depending on the location. The experiments were made using 3% salt solution in steel trays of area five sq.ft. Neville Jones[148] calculated the respective costs of reducing a salinity from 20,000 p.p.m. to 300 p.p.m. to be £0·11, £0·26 and £0·13 per ton by distillation, solar distillation and electrodialysis respectively, operating on a scale of a thousand tons a day.

The problem of desalting crude petroleum oil has been reviewed by Foster.[151]

The salt content of agricultural land that has been flooded by sea water is important in that too much sodium chloride gives poor crops in many cases. Claerhout[152] has shown that flooded land recovers much more quickly after treatment with calcium chloride or lime. This is in agreement with earlier work.[153] Christensen[154] has reviewed the extent to which sodium chloride impairs the growth of many root crops.

In connection with the desalinification of sea water by ion exchange resins, the recovery of the salts so removed is possible. Three Japanese patents[155-157] discuss the application of cation-exchange resins to the production of sodium. Two of these[156,157] develop the process to recover magnesium also.

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PHYSICAL PROPERTIES OF SODIUM CHLORIDE

By J. M. THOMAS

Crystal Structure of Sodium Chloride

It has been shown on numerous occasions that the crystal structure of sodium chloride is face-centred cubic, and the methods employed to establish this fact have simultaneously revealed information relating to the lattice spacing, electron density distribution, percentage ionic character, mosaicity and the lattice vibrations of the solid.

Ever since W. H. and W. L. Bragg discovered that a crystal could behave as a three-dimensional diffraction grating, there has been a steady stream of investigations dealing particularly with the diffraction of *X*-rays by rock salt and sodium chloride. Since 1921 there have been very many *X*-ray studies of the sodium chloride crystal structure in which the von Laue single crystal method, the rotating crystal method, and the Debye-Scherrer-Hull powder method have been used.[1-26] Several reviews of the methods of *X*-ray diffraction as applied to crystal structure determination have been given,[14,15,24,25] and general discussions are available on the Fourier synthesis and Patterson-Harker synthesis methods of calculating the electron density distribution[27-30] and on the method of obtaining the mosaic structure of the salt by means of *X*-ray reflection experiments.[31-34]

X-Ray reflection photographs of single crystals of rock salt display diffuse spots which are not part of the normal Laue pattern.[35-48] The intensity of these spots increases as the temperature is raised to about 500°C.[35,41] The origin of the phenomenon has been much discussed. Zachariasen[37] and Jahn[49] attributed the diffuse scattering of *X*-rays by rock salt and sodium chloride (and of other solids which give rise to the effect), to thermally excited lattice vibrations. This interpretation was challenged by Raman[45,46] and Venkateswaran,[47] who maintained that the extra Laue spots observed in *X*-ray spectra were due to the infra-red or characteristic high frequency vibrations of the crystal lattice. Verkateswaran[47] produced experimental evidence which ostensibly supported the infra-red vibration theory, but Lonsdale[48] has shown that these experimental observations were invalid and that the usual inter-

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pretation, *viz.* the thermal vibration theory is in better accord with the experimental facts. The magnitude of the thermal vibrations can be gauged from the results of Wasastjerna[44] who calculated the mean squares of the amplitudes of the vibrations of the atoms to be 0·243 A. and 0·234 A. for the sodium ions and chloride ions respectively.

A general theoretical investigation on the relation between crystal dynamics and *X*-ray scattering and an experimental study of *X*-ray scattering in relation to crystal dynamics with special reference to sodium chloride were carried out by Born[50] and Lonsdale,[51] respectively, in 1942.

The crystal structure of sodium chloride constructed from the results of *X*-ray diffraction experiments has been amply vindicated by other methods such as electron diffraction,[52-60] the reflection of beams of inert atoms,[61] neutron diffraction[62] and nuclear magnetic resonance.[63,64] The last-named method gives a value of about 99% for the ionic character of the Na–Cl bond in the crystal.[63]

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The Growth of Sodium Chloride Crystals

The subject of crystal growth is almost as old as chemistry itself (Partington, An Advanced Treatise on Physical Chemistry, Vol. III, p.12). It continues to elicit an abundance of publications dealing with both its theory and its practice, these being of immense importance to the solid state physicist and the physical chemist alike.

In the following account emphasis is placed mainly on the purely practical aspects of sodium chloride crystallization since comprehensive reviews.[1-9] of theoretical and practical considerations are available elsewhere. For example, a Discussion of the Faraday Society treats fully the growth of many types of crystal in contact with vapour, solution and melt; an article by Frank[2] deals with the growth of imperfect crystals, mainly from the theoretical standpoint; Buckley[3] considers at length crystal habit and morphology and Saratovkin[9] dendritic crystallization.

Crystallization from Aqueous Solutions of Pure Sodium Chloride.

It has long been known that the external shape of a sodium chloride crystal depends on the conditions under which it is formed. Thus, it is possible to produce at will hollow pyramidal,[10,11] needle-shaped,[12,13] or dendritic[9,14] crystals. Crystallization may be effected by adding a common ion[15] or by cooling[16-18] or evaporating[19,20] an aqueous solution. The degree of supersaturation,[21,22] and also the rate of addition[15] of common ion, or rate of cooling[18] or evaporation[20] play an important part in modifying the habit of the crystal, e.g. slow evaporation of an aqueous solution of sodium chloride heated on a glass or platinum slide gives a preferred orientation of the (100) faces.[20] The effect of supersaturation on the crystal habit is, in practice, well understood.[22-25] At concentrations close to saturation crystals of (100) habit appear; with greater supersaturation dendrites appear; and at still higher supersaturation the (111) faces appear which also become dendritic at the maximum value of supersaturation.[24,25] If the process of crystallization of sodium chloride from saturated solution is thrown out of balance by supersaturating at the instant of crystallization, complications such as crystal twinning may be produced.[26,27] (For a survey of twinned crystals, which deals especially with growth twins, see the article by Cahn.[28])

The crystallization of sodium chloride in the presence of heavy water (D_2O) favours the formation of numerous small crystals.[29]

Crystallization from Solutions Containing Other Species.

Many examples are known of the profound effect of small quantities of inorganic impurities, present in aqueous solutions of sodium chloride, on the opacity, size and shape of the final crystal. Manganous ions (0·01 to 0·001 g. ions $l.^{-1}$) facilitate the crystallization of large, transparent crystals during the slow evaporation of a saturated solution.[30-32] Traces of manganous chloride, cadmium chloride and zinc chloride promote the crystallization of octahedral crystals of sodium chloride.[33] In solutions containing high concentrations of magnesium chloride the development of the (110) face is favoured at the expense of the (210) face in growing sodium chloride crystals,[34] whereas in the presence of bismuth ion small cubes of sodium chloride are first formed; these become pyramidal, and the base of the pyramid then extends diagonally giving finally star-like crystals.[35]

The foreign ions present in a crystallizing solution are often carried down by the sodium chloride crystal: the existence of the Fajans–Paneth Precipitation and Adsorption rules clearly demonstrates that this is a well-recognized phenomenon. When cadmium ions are present at a concentration of less than 1 p.p.m. of crystallizing solution, they are carried down almost completely by the first 5% of the crystals.[36] Lead ions behave similarly, but ions of zinc, manganese or bismuth will remain completely in solution.[36] Not only do cadmium and lead ions cocrystallize with sodium chloride, they also modify the crystal habit and slow the rate of crystallization.[37] There is little doubt that the small amounts of plumbous chloride found in sodium chloride and potassium chloride of oceanic origin are the end-products in the disintegration of radioactive salts which were cocrystallized with the alkali metal chlorides.[38] Optical transmission data reveal that the lead impurity in sodium chloride is not dispersed atomically in a random manner within the lattice but occurs in aggregates.[39]

Crystallization of sodium chloride from aqueous media is affected equally profoundly by the presence of organic impurities of which the most widely studied is urea.[40-45] With high concentrations of urea, the growth velocity of sodium chloride is greatest on the (111) face: this holds down to concentrations of 8·5 g. of urea per 100 $cm.^3$ of solution.[41] From this concentration down to 5 g. per 100 $cm.^3$ the growth velocity is about equal on the (100) and (111) faces, and below the latter concentration the (100) face is preferentially developed.[40] The influence of glycine, 12 g. of which in 100 g. of saturated solution favours the crystallization of rhombic dodecahedra, may be interpreted in terms of its adsorption on edges of (100) faces.[43] The presence of gelatin or agar-agar results in a greater tendency to dendritic crystallization of sodium chloride, but this effect can be suppressed if, in addition to the organic molecule, small quantities of ferric chloride, cobaltous chloride or nickelous chloride are present.[46,47] The limiting concentrations of ferric, cobaltous and nickelous chlorides which cause complete disappearance of the sodium chloride dendrites in the presence of gelatin and their replacement by sodium chloride cubes are 0·010, 0·126 and 0·124 mole $l.^{-1}$ respectively. Pyridine, betaine and β-alanine in aqueous solutions of sodium chloride also modify the habit of the growing crystal.[48]

The influence of foreign substances on the crystallization of sodium chloride from brines[49,50] and sea water[51] has also been studied.

The crystallization of the salt from various organic solvents is known to be sensitive to additions of both organic and inorganic substances[52,53] - but this subject has received scant attention.

Conditions for the optimum crystallization of solid solutions containing sodium chloride have been ascertained for the following systems: sodium chloride–sodium bromide–water,[54–57] sodium chloride–sodium bromide–sodium iodide–water,[54] sodium chloride–sodium bromide–sodium iodide–potassium chloride–water,[57] sodium chloride–magnesium chloride–magnesium bromide–water,[57] and sodium chloride–sodium bromide–sodium iodide–water.[58]

Other Methods of Growing Sodium Chloride Crystals.

Besides the crystallization of the salt from its solutions, there are two other methods of generating sodium chloride crystals - from the melt, and from the vapour phase.[1,3]

By using the first of these alternatives, it is possible to produce very large single crystals which are ideal for use in infra-red spectroscopy and in the study of luminescence (q.v.). Single crystals of sodium chloride in the form of cylindrical bars (e.g. 2 cm. diameter and 30 cm. long) may be obtained by the controlled, continuous lifting of the growing crystal by means of a platinum rod from the molten salt.[59–61] Large crystals of the order of 25 cm. diameter and 12 cm. in height may also be obtained by floating the growing crystal on the surface of the melt kept in a furnace the temperature of which is gradually lowered by about 20°C. during a two-week interval.[62,63] The advantages and limitations of these two techniques have been discussed,[61,63] and particular attention has been given to the rejection of foreign ions, which may be present in the melt, by the growing sodium chloride crystal.[60]

Single crystals of sodium chloride–potassium chloride solid solution have been prepared by slowly cooling the mixed melt to 600°C.[64] The kinetics[65] of such a crystallization and a theoretical model of the mechanism[66] have been reported. Some data on the crystallization of sodium chloride–silver chloride solid solutions are also available.[67]

The second of the above alternatives, deposition from the vapour phase, is now being used increasingly as a convenient method of preparing samples of sodium chloride possessing large surface area. de Boer[68] succeeded in condensing the salt from the vapour phase on a cool surface in high-vacuum under conditions which avoided collisions of the salt in the vapour phase. By this means, he was able to obtain two-dimensional nuclei which grew two-dimensionally.[68] Craig and McIntosh[69] prepared sodium chloride samples ranging in surface area from 7·1 to 54·4 m.^{2}g.$^{-1}$ by evaporating the solid at 750°–850°C. and collecting the smoke particles in an electrostatic precipitator carrying a p.d. of 2000 V. Another method,[70] which also employs the principle of electrostatic precipitation, can produce crystals of mean particle size in the range 0·01 to 1·0 μ at rates of 0·8 g.hr.$^{-1}$, the surface area being as large as 64 m.^{2}g.$^{-1}$

Crystal growth from the vapour phase is further considered below.

Epitaxy.

Epitaxy, or oriented growth of one crystal upon another, is a subject which has flourished in recent years with the development of powerful techniques of electron diffraction, X-ray diffraction, and electron microscopy. The growth of a number of metals has been studied but by far the greatest interest has been focused on the growth of alkali metal halides on other alkali metal halides as well as alkali metal halide growth on metals.

Whilst current interest in this subject seems to be directed more to the study of oriented growth from the vapour phase,[71–73] some data on oriented growth of crystals from aqueous solutions[74–79] and melts[71] are also available. Pashley[71] has reviewed this subject fully, and many of the systems listed here are discussed in his article in greater detail. Studies have been made of the epitaxial growth of sodium chloride deposited from the vapour phase on sodium chloride itself,[78,79] potassium chloride,[79,80] lithium fluoride,[79] potassium bromide,[80] rubidium chloride,[71] rubidium bromide,[71] cæsium chloride,[81] potassium iodide,[71] ammonium iodide,[71] rubidium iodide,[71] mica,[71,82,83] calcite,[71,84] sodium nitrate,[71,84] metallic copper,[85,86] platinum,[85] aluminium,[85] silver,[71] galena,[87] glass,[86] organic plastics[86] and celluloid.[88] Epitaxy of sodium chloride crystallized from solution on to metallic silver,[75,76] copper,[75] antimony,[75] bismuth,[75] zinc,[75] lead,[71] gold[71] and cleaved crystals of the colloxides of bismuth,[75] sodium,[75] potassium[75] and rubidium[71,75] has also been studied.

When sodium chloride grows on other alkali halide crystals, epitaxy will occur on whichever cleavage face of the substrate is exposed.[71] At one time it was suspected[71,89] that one of the conditions for epitaxy was parallelism of the two lattice planes, *i.e.* oriented growth would not occur unless the lattice plane of the substrate had a network identical or nearly identical in form with that of the condensate, and closely similar in spacing. Expressed quantitatively, early experiments indicated that the percentage misfit between the corresponding networks should be no more than about 15%. The percentage misfit is defined as $100(b-a)/a$, where a and b are the network spacings in the substrate and overgrowth respectively.[71] Schultz's work[71,79] has shown quite incontrovertibly that epitaxy occurs independently of misfit in the alkali halide systems studied by him. While this may not be absolutely true for sodium chloride growing on any other alkali metal halide substrate, it appears certain that misfit plays only a secondary role. The epitaxial growth of sodium chloride from solution on alkali halide substrates is influenced by the nature of the solvent: a reduction in the dielectric constant of the solvent increases the probability of orientation.[71]

The most commonly occurring epitaxial growth of sodium chloride on muscovite mica,[71,82,83] has a (111) plane of the halide parallel to the (001) mica cleavage surface, with the $(1\bar{1}0)$ or $(\bar{1}10)$ directions in sodium chloride parallel to the mica (100).[71] Such oriented crystals are visible under the optical microscope, appearing as (111)-based triangular pyramids. In this particular instance, the percentage misfit is −23%.

In the principal type of orientation of sodium chloride overgrowths on calcite and sodium nitrate,[71,84] the percentage misfit is −13%. The results of the measured epitaxy of sodium chloride on etched polycrystalline metal surfaces, etched massive single crystal surfaces, and oriented metal layers formed on other single crystal substrates have been summarized by Pashley.[71]

Although no satisfactory general theory of epitaxial growth that can account for all the experimental facts has so far emerged, it may be stated[71] with reasonable certainty that: (i) it is not essential for only a small misfit to exist between substrate and overgrowth; (ii) the actual orientation that occurs is not always that corresponding to the best geometrical fit, and (iii) the assumption that an intermediate orientation of smaller misfit occurs as a precursor of orientation involving larger misfit, does not satisfactorily explain many cases of observed large misfits.

As to the mechanism of epitaxial growth, there are two distinct possibilities: the 'gradual nucleation' mechanism and the 'spontaneous nucleation' mechanism. Some of the evidence now extant tends to favour the latter.[71]

All the foregoing comments apply equally to epitaxial growth of other substances on rock salt and sodium chloride substrates. In this category, overgrowths of metals on rock salt have been most frequently studied, the majority of the metals being deposited from the vapour phase. Data concerning the following metals have been reported: silver,[90-99] palladium,[90,95] gold,[90,100] aluminium,[90] copper,[90,101,102] cobalt,[90] nickel,[90] iron,[90] chromium[71,90] and molybdenum.[71] The epitaxy of ammonium bromide[103] and many other alkali metal halides on halite and sodium chloride has been observed.[71] Some facts are also known about epitaxial growth of layers formed on a sodium chloride surface by a chemical reaction of the surface with its environment[104-106] e.g. the growth of plumbous chloride formed on heating sodium chloride on to which lead sulphide has been deposited.^{104}

The study of epitaxy is now being extended to the field of organic deposits on inorganic substrates. The epitaxial growth of ordinary, commonly-occurring organic species such as naphthalene, anthracene, hexamethylenetetramine, benzoquinone, *o*-aminophenol, *p*-aminophenol, and dimethylglyoxime on rock salt,^{107,108} and of organic high polymers such as polyethylene on sodium chloride^{108} has already been studied.

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Lattice Constant and Lattice Energy of Sodium Chloride

The dimensions of the unit cell of the face-centred cubic sodium chloride crystal have been measured on many occasions, chiefly by the *X*-ray diffraction method. Table X summarizes the results obtained since 1922; it also shows that the lattice constant, a ($2a = c$, the distance between ions of the same kind), varies very slightly from specimen to specimen depending on whether the latter is natural or synthetic, pure or impure, powdered or in the form of a single crystal.

TABLE X.- DIMENSIONS OF SODIUM CHLORIDE UNIT CELL

c (A.)	Type of Specimen	Temp. °C.	Method Used	Ref.
5·62710	Rock Salt	Room Temp.	*X*-ray Diffn.	1
5·6294±0·0018	Rock Salt	20	*X*-ray Diffn.	2
5·628	Sodium Chloride	Room Temp.	*X*-ray Diffn.	3
* 5·628	Rock Salt	Room Temp.	*X*-ray Diffn.	4
* 5·626	Sodium Chloride	Room Temp.	*X*-ray Diffn.	4
5·6264±0·0003	Sodium Chloride	Room Temp.	*X*-ray Diffn.**	5
$5{\cdot}6273_7 \pm 0{\cdot}0000_2$	Sodium Chloride	Room Temp.	*X*-ray Diffn.**	6
σ $5{\cdot}6276_8 \pm 0{\cdot}0000_5$	Rock Salt	Room Temp.	*X*-ray Diffn.**	6
θ $5{\cdot}6274_7 \pm 0{\cdot}0000_3$	Rock Salt (powder)	18	*X*-ray: powder	7
θ $5{\cdot}6273_5 \pm 0{\cdot}0000_2$	Rock Salt (single crystal)	18	*X*-ray Diffn.	7
5·62869±0·00006 kX[a]	Sodium Chloride	Room Temp.	*X*-ray Diffn.	8
5·529	Sodium Chloride	Room Temp.	Electron Diffn.	9,10
5·63978	Sodium Chloride	18	*X*-ray Diffn.	11

[a] 1 kX unit ≡ 1·00202 A.
* Difference attributed to small quantities of potassium chloride in natural rock[4] salt.
σ Rock salt taken from three different sources.
θ The difference of 0·00012 A. can be attributed to line displacement through absorption in the single crystal and through the glowing of the powder.[7]
** Debye–Scherrer.

It was at one time believed[9,12-14] that the lattice constant determined using the electron diffraction method differed slightly, but quite definitely, from that obtained by *X*-ray diffraction. This is erroneous, and the issue was resolved by Boswell.[13] He found that the lattice constant of sodium chloride, like that of five other alkali metal halides, agrees within an experimental error of 0·05% with the corresponding *X*-ray value, provided the crystallites of the salts are greater than 150 A. in diameter. For crystal sizes less than 100 A., the lattice constants of the alkali metal halides are less than the *X*-ray values by an amount dependent on crystal size, e.g. for a crystallite size of approx. 30 A., the decrease is nearly 0·5%.[13] Such effects can be interpreted in terms of the increasing influence of surface energy with decreasing crystallite size.[15]

X-Ray diffraction patterns of powdered sodium chloride specimens which have been subjected to pressures of 12,300 to 23,300 atm. in oil for 100 min. to 36 hr. followed by draining, show a slightly smaller lattice parameter.[16] This lattice contraction, which is still discernible eight months after the compression, is rendered possible by the original imperfection of the lattice together with the ability to undergo viscous flow.[16]

During *X*-irradiation at room temperature a crystal of sodium chloride expands as well as developing colour. (See page 805) Sakaguchi and Suita[17,18] discovered this, and noted that expansion starts as soon as irradiation begins. For the first hour or so the expansion varies linearly with time but eventually, after some five hours, the expansion slows and approaches the asymptote. The *X*-rays used were sufficiently hard to penetrate for distances of the order of tenths of a millimetre, and the final increase in linear dimensions corresponded to the production of about $1{\cdot}2 \times 10^{18}$ vacancy pairs cm.^{-3}, if the latter were the major source of volume change.[18] In all probability this lattice expansion is, as assumed, associated with the production of vacancy pairs, and is not likely to be connected with other possibilities such as salt decomposition followed by increased porosity, because the estimated density of *F*-centres (see page 806) is consonant with the above value for the volume concentration of vacancy pairs.[18]

The distinction between a unit cell and a unit cube in any crystal has been discussed and illustrated by reported data on sodium chloride.[19]

Lattice Energy.

As sodium chloride is one of the simplest polar crystals known, its lattice energy has been the subject of very many theoretical calculations.[20-32] To calculate the sodium chloride lattice energy, which may be looked upon as the free energy change accompanying the formation of one mole of the lattice from gaseous sodium and chloride ions at infinite distances apart, it is necessary to calculate first the electrostatic energy, the repulsion energy, the van der Waals energy, the zero point energy and the influence of the polarizibility of the ions. The calculations of all these energies have been fully treated in texts by Partington (An Advanced Treatise on Physical Chemistry, Vol III), Seitz[33] and Kittel.[34]

The Madelung constant, α_M, for the rock salt lattice enters into the calculation of the electrostatic energy and is defined by: $\phi = -(Ze\alpha_M)/r$ where ϕ denotes the electrostatic potential at any lattice point of the crystal due to all the ions except the one occupying that point, $\pm Ze$ are the charges on the ions ($Z = 1$), and r is the inter-ionic distance. The value of α_M for the rock salt lattice is 1·747558, referred to the smallest distance between neighbouring ions. (If the value chosen for the unit distance in the rock salt type lattice is the shortest distance between ions of the same kind, the value of α_M then becomes 3·495115).[34-37]

Typical results derived theoretically for the lattice energy are 183·1 and 178·0 kg.-cal. mole^{-1}.[34] The mean of the experimentally determined values is 182·8 kg.-cal. mole^{-1}.[33,34,38]

Comparisons have been drawn between the experimental and theoretical lattice energies of various mixed crystals containing sodium chloride. Reasonable success has been achieved, but further refinements of the theoretical models are necessary before the small changes in lattice spacings and energy content that accompany the formation of solid solutions can be accounted for completely. Binary systems that have received detailed consideration are sodium chloride–potassium chloride[39-42] and sodium chloride–sodium bromide.[40,43-46]

Using the Matt and Littleton crystal model,[47] Brauer[48,49] has made numerical calculations to show that it is not energetically feasible to insert a thallous ion, Tl^+, in place of a sodium ion in the sodium chloride lattice. It is, on the other hand, energetically feasible for a thallous ion to be accommodated in place of a potassium ion in the potassium chloride lattice. Therefore, the fact that solid potassium chloride containing thallium crystallizes from a potassium chloride–thallous chloride aqueous solution, whereas sodium chloride free from thallium crystallizes from a sodium chloride–thallous chloride solution, may be readily explained.[48,49] By an analogous calculation[50] it can be shown that the inclusion of the manganous ion, Mn^{2+}, in the sodium chloride lattice is favoured, whereas the inclusion of the same ion in the potassium chloride lattice is not.

Thermal Expansion of Sodium Chloride.

Accurate values for the coefficient of thermal expansion of sodium chloride are available from low temperatures[51,52] (approx. −170°C.) to about 800°C.[53,54] As for any crystalline solid, the expansion coefficient of sodium chloride tends towards zero at very low temperatures and changes more rapidly with temperature than does the specific heat.[51] The total expansion of rock salt from 0° up to the m.p. is approx. 6%.[53] Natural and synthetic sodium chloride differ in their expansion coefficients by as much as 5%.[54,55] The following formula describes the coefficient of linear expansion, α, of sodium chloride:[56]

$$\alpha = 40{\cdot}31 \times 10^{-6} + 33{\cdot}71 \times 10^{-10}t + 63{\cdot}46 \times 10^{-12}t^2 \quad (t = {}^\circ\text{C.})$$

Attempts[34,57-60] to construct an equation of state for solid sodium chloride have led to the derivation of theoretical expressions for the linear coefficient of expansion. In this connection, much use has been made of the Gruneisen relation:[34]

$$\alpha = (K\gamma C_V)/3V, \dots\dots\dots(1)$$

where K is the compressibility coefficient (q.v.), C_V the specific heat at constant volume, V is the volume and γ is the Gruneisen constant which has a fixed value for a particular substance and is temperature-independent. This equation is satisfied experimentally for cubic crystals.[34] Two values of γ for sodium chloride are in use: 1·52 calculated by Slater, and the value, 1·63, obtained experimentally assuming the validity of equation (1).[34]

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Density

Solid.

Table XI summarizes the earlier and more recent values obtained for the density of rock salt.

TABLE XI.- THE DENSITY OF ROCK SALT

Investigators	Date	Type and purity of sample	Density (g./c.c.)	Temp.°C.
Geiss[1,2]	1924-5	Stassfurt and Friedrichschall rock salt (99·7–99·8%)	2·1644±0·5%	18·0
Defoe and Compton[3]	1925		2·1632±0·0004	20·0
Batuecas and Casado[4]	1937		2·1675±0·0001	0·0
Johnston and Hutchinson[5]	1942	'Purified' crystals	2·16171±0·00002	27·63
			2·16372±0·00003	20·0
Casado[6]	1945		2·1683±0·0001	4·0
			2·1635±0·0001	18·0
Lopez-Rubio and Pacheco[7]	1950	Rock salt (99·98%)		
		Blue crystals	2·262	
		Transparent crystals (*a*)	2·2779	
		Transparent crystals (*b*)	2·164–2·174	

continued on following page

TABLE XI continued

Investigators	Date	Type and purity of sample	Density (g./c.c.)	Temp. °C.
Alonso, et. al.[8]	1951	Salt cooled slowly from melt	2·16875 ±0·00015	4·0
		Salt cooled rapidly from melt	2·16669	4·0
Batuecas and Carreira[9]	1955		$2{\cdot}1638_7$	23·5

(*a*) These crystals give a pepperlike taste before the salty taste is experienced.
(*b*) These were crystals with no pepperlike taste.

Geiss[1] gives the equation relating the density of solid sodium chloride, d_t, to the temperature, t(°C.) as:

$$d_t = 2{\cdot}1644[1-0{\cdot}000121(t-18{\cdot}0)]$$

Recently the densities of molten salt mixtures of the system NaCl-KCl-$CaCl_2$-$MgCl_2$ in the temperature range 675° to 856°C. have been determined,[10] the results being expressed graphically.

Solutions.

Accurate data on the densities of sodium chloride solutions have been published since 1924.[11-13] Root's equation:[13]

$$d = d_0 + pN + qN^{3/2},$$

in which d_0 is the density of pure water and p and q are constants, N being the normality, is accurate within the limits of experimental error for solutions of alkali halides (except lithium) up to a concentration at least as high as 10 N. Bremner, *et al*,[14] have determined the values of the constants p and q at various temperatures for sodium chloride solutions and for aqueous NaCl-KCl and NaCl-$MgSO_4$ solutions. Their data for the sodium chloride solutions are reproduced in Table XII.

TABLE XII.- CONSTANTS OF ROOT'S EQUATION FOR SODIUM CHLORIDE

Approx. no. of mg. eq. wts. per litre soln.	°C.	p	q
100–500	25	0·04196	−0·001853
	20	0·042432	−0·001990
	15	0·042995	−0·002052
	10	0·043740	−0·002204
	5	0·044660	−0·002391
	0	0·045846	−0·002684

Using the above constants, the agreement between the observed and calculated values is in every instance within 5 units in the sixth decimal place.

A simple formula relating the density of sodium chloride and potassium chloride solutions at identical concentrations and at 20°C. is:

$$(d_{NaCl} - d_0)/(d_{KCl} - d_0) = 1{\cdot}12;$$

d_0, the density of water, is 0·9982 at this temperature. This principle holds for about forty other salt pairs up to certain limiting concentrations.[15]

The densities of liquid ammonia solutions of sodium chloride and mixtures of sodium chloride and ammonium chloride in liquid ammonia, including the values for the saturated solutions for each case, have been determined.[16]

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Vapour Pressure and Heats of Vapourization

Pure Sodium Chloride.

The vapour pressure data[1,2] for crystalline sodium chloride between 750° and 890° K. fit the equation:

$$\log_{10} p_{(\mathrm{mm})} = C - A\left(\frac{1000}{T}\right) + 2\log_{10}\left(\frac{1000}{T}\right),$$

the values of A and C being 12·288 and 11·093 respectively.[2] The above vapour pressure data when recorded on a $\ln p - 1/T$ graph yield the following values for the heat of vaporization expressed in kg.-cal. mole.$^{-1}$

$$\Delta H\,(\text{at } 800^\circ\text{K.}) = 53{\cdot}02 \pm 0{\cdot}47$$
$$\Delta H\,(\text{at } 0^\circ\text{K.}) = 55{\cdot}32 \pm 0{\cdot}50$$

From 890·2° to 944·1°K., the vapour pressure of solid sodium chloride, which varies from $2{\cdot}11 \times 10^{-3}$ to $10{\cdot}5 \times 10^{-3}$mm. Hg, is best expressed by:[1]

$$\log_{10} p_{(\mathrm{mm})} = -\frac{A}{T} - 3\log_{10}\left(\frac{T}{1000}\right) + C,$$

where A is 12629 and C is 11·345. Mayer and Wintner[1] have analyzed their own data and the results of previous investigations, and thus derived the most probable value for the heat of vaporisation at 900°K., this value being the weighted average of three different methods of calculation. The first and least accurate method uses the Clausius–Clapeyron equation over a restricted temperature interval:

$$\Delta H_{\text{vap.}}\ (900^\circ\text{K.}) = 50{\cdot}5 \pm 2{\cdot}5 \text{ kg.-cal. mole}^{-1}$$

The second method incorporates the results of other workers on the vapour pressure of solid and liquid sodium chloride; the Clausius–Clapeyron equation then yields 53·6±1·5 kg.-cal. mole^{-1}. Thirdly, $\Delta H_{\text{vap.}}$ at 900°K. is calculated from the Gibbs–Helmholtz equation:

$$-\Delta G_v = RT\ln p = -\Delta H_v + T\Delta S_v,$$

one measurement of pressure being used to determine ΔG_v, the Gibbs free energy of vaporization. The entropy of vaporization at 900°K., ΔS_v, was obtained by subtracting from the entropy of gaseous sodium chloride, calculated in turn from the fundamental frequency of the gaseous halide, the entropy of the crystalline salt at 900°K. The latter quantity was obtained from the measured entropy at room temperature and specific heat data. This procedure gives $\Delta H_{\text{vap.}}$ at 900°K. = 52·4 ± 1·7 and this figure is also the weighted average of the three values obtained. Also $\Delta H_{\text{vap.}}$ at 0°K. was calculated to be 55·2 ± 2·0 kg.-cal. mole^{-1}.

The equation:

$$\log_{10}p = -\frac{A}{T} + B,$$

where A is 8475 and B is 7·906, expresses satisfactorily the vapour pressure of molten sodium chloride from 1133° to 1263°K.[3] The heat of vaporization at 1198°K. (*i.e.* from the liquid state) calculated from the last equation is 39·7 kg.-cal. mole^{-1} which agrees well with an earlier value[4] 39·6 kg.-cal. mole^{-1} also derived from vapour pressure measurements. Vapour pressures of molten sodium chloride from 1264° to 1514°K.[4] are as follows:-

T(°K.)	P(mm. Hg)
1264	15·0
1314	22·5
1364	39·5
1414	61·5
1464	100·0
1514	149·0

Vapour pressure–composition curves for the following binary mixtures have been determined at high temperatures: sodium chloride–potassium chloride[5,6] (under nitrogen[5]); sodium chloride–sodium iodide;[6] sodium chloride–lithium chloride;[3] sodium chloride–rubidium chloride[3] and sodium chloride–cæsium chloride.[3] In the temperature interval 1133°–1263°K. the Gibbs–Duhem equation appears to be valid, but the course of the partial-pressure curves[3] indicates that the melts do not behave as ideal solutions.

The effect of gaseous media on the volatility of solid sodium chloride at 800°C. has been studied by passing controlled volumes of air, water vapour and gaseous ammonia over a platinum boat filled with the salt and determining the weight loss.[7,8] The rate of evaporation is identical for all gases when the gas flow rate is less than 12·0 l./hr. With a flow rate of 24·0 l./hr., however, the rate of evaporation increases in proportion to the polarity of the gas used, this effect being smaller for sodium chloride than for all the other alkali chlorides. When about 0·25 g. of sodium chloride is exposed to air at 750°C. the rate of evaporation, expressed[8] as percentage loss of weight in 1 hr., is 0·62. The rate of evaporation of a similar sample, in the same units, when exposed to a stream of gaseous hydrogen chloride at 10 l./hr. is 0·48, and in a stream of water vapour (6 l./hr.) the rate is[8] 0·58.

Aqueous Sodium Chloride Solutions.

Several determinations of the vapour pressures of unsaturated and saturated aqueous solutions of sodium chloride have been carried out since 1920.[9-18] Table XIII lists the vapour pressures of saturated sodium chloride solutions determined by means of the static method with an accuracy of about 0·05 mm. Hg. Each solution was kept at constant temperature for at least 24 hr. before the vapour pressure was recorded.[18] Further data,[19] obtained using the gas saturation method, are shown in Table XIV. The errors in the vapour pressure lowering data are, throughout, between 0·003 and 0·004.

When a selection of other published values is incorporated into the results included in Table XIV and a graph of $(p_0 - p)p_0$ against molality is con-

TABLE XIII.- VAPOUR PRESSURE OF SATURATED AQUEOUS SODIUM CHLORIDE SOLUTIONS

Temp. °C.	Moles Salt per 1000 g. water	Vapour Pressure		$\Delta = \frac{p_0 - p}{p_0 M}$
		water (P_0)	soln. (P)	
20·42	6·130	18·19	13·65	0·04073
25·49	6·148	24·45	18·35	0·04057
29·96	6·167	31·75	23·80	0·04060
36·92	6·201	46·86	35·03	0·04070
40·55	6·220	56·96	42·54	0·04070
50·00	6·227	92·51	68·84	0·04077

TABLE XIV.- VAPOUR PRESSURE OF SODIUM CHLORIDE SOLUTIONS AT 30·01°C.

Molality	Vapour Pressure Lowering $(p_0 - p)/p_0$
3·753	0·139
4·563	0·174
4·910	0·190
5·070	0·196
5·162	0·200
4·910(at 25·00°C.)	0·185

structed, a perfect straight line is obtained, indicating that Raoult's law is obeyed.[19]

An ingenious method, devised by Sidgwick and Ewbank[20] in which the vapour pressure of an aqueous salt solution is measured by the lowering of the solution produced in the freezing point of an organic liquid in contact with it, yielded the equation:

$$\frac{p}{p_0} = 2{\cdot}164d - 0{\cdot}05d^2 + 0{\cdot}22d^3$$

in which p is the vapour pressure of the solution, p_0 the vapour pressure of pure water, and d the freezing point depression of nitrobenzene in contact with the solution. This equation was derived on the basis that the freezing point of benzene is 5·493°C. and that of nitrobenzene 5·689°C. p/p_0 was determined for several concentrations of aqueous sodium chloride.

Graphical data on the vapour pressures of the sodium chloride-water system from 183° to 646°C. have been compiled by Keevil[21] who observed that a maximum in the vapour pressure occurs at a temperature intermediate between the triple points of water and sodium chloride. This occurs generally for aqueous solutions of salts that are highly soluble,[22] and it has been possible to calculate, assuming that the solutions are ideal, that $T_{\text{max.}}$, the absolute temperature of the maximum in the vapour pressure, is related to the melting point T_s (°K.) of the salt by the equation:

$$\frac{1}{T_{\text{max.}}} = \frac{1}{T_s} + 0{\cdot}00021$$

Thus, for sodium chloride the observed $T_{\text{max.}}$ is 600°C. while that calculated from the melting point using the above equation is 606°C. Sodium bromide and potassium chloride also conform to this equation, and it also applies to the vapour pressure curves of solutions saturated with respect to two or more salts, in which case T_s is now the eutectic temperature of the salt mixture.[22]

The relative humidity above a saturated solution, sometimes called the 'hygroscopic point', H, varies continuously as a function of temperature. The curve for saturated sodium chloride solutions between 0° and 50°C. rises from 74·9% relative humidity at 0°C. to a maximum of 75·6% at 30°C. and then gradually falls to 74·7%.[23] Determinations of the 'hygroscopic point' of saturated sodium chloride solutions to an accuracy of 1 to 1·2% give values which compare favourably with the above.[24,25] Thus H, which is readily obtained from the vapour pressure, p, of a saturated solution and the vapour pressure p_0 for pure water by means of the formula $H = 100p/p_0$, is 75·8% at 20°C. For the range 0–100°C., $\log H = 1{\cdot}8736 + 12{\cdot}283/T$, where T is the absolute temperature.

To obtain the osmotic properties of aqueous solutions of mixed salts many accurate isopiestic measurements have been performed. Although most of the pertinent original papers tabulate mainly the osmotic coefficients, ϕ, or the mean activity coefficients, $\gamma_\pm$, of the solute at various molalities, m, and do not record directly the vapour pressures of the solutions, the latter can be calculated from the equations:

$$\phi = -\frac{(55{\cdot}51)\ln a_w}{\nu m}$$

and

$$d(\ln\gamma_\pm) = -\left(\frac{1}{m}\right)d\{m(1-\phi)\},$$

where ν is the number of ions per mole of electrolyte and a_w is the activity of the water, *i.e.* the vapour pressure of the solution divided by the vapour pressure of pure water.

Isopiestic measurements have been carried out on mixed sodium chloride-potassium chloride solutions at 25°C. at concentrations from 0·03 to 0·10 molal[26] as well as on aqueous sodium chloride–lithium chloride mixtures at the same temperature.[27]

The vapour pressure of a solution of the salt $CuCl_2,2NH_4Cl,2H_2O$ with sodium chloride added until a saturated solution is obtained has been found to be 12·73 mm. Hg at 19·93°C. Vapour pressure data are available for solutions containing varying amounts of sodium chloride, ammonium chloride and $CuCl_2,2NH_4Cl,2H_2O$,[28] as well as vapour pressure-composition curves for the following more complicated systems: ethanol-water-sodium chloride (at 30°C.),[29] glycerol-water-sodium chloride,[30] magnesium chloride-water-sodium chloride (at 25°C.)[31] and sodium sulphate-water-sodium chloride also at 25°C.[31] A table has been constructed giving the molalities of sodium chloride solutions that have vapour pressures equal to those of sea waters at 25°C. possessing a chlorinity range of 1·0 to 2·2%.[32]

Attempts to calculate the vapour pressure of aqueous sodium chloride solutions by extending the Maxwell theory of distribution of molecular velocities,[33] and by using the generalized form of Raoult's equation[34] have proved moderately successful.

When sodium chloride is recovered from saturated solutions of rock salt ($NaCl$ 97·81, KCl 0·87, $MgCl_2$ 0·18, $MgSO_4$ 0·37, $CaSO_4$ 0·66, and $Ca(HCO_3)_2$ 0·08%),[35] the rate of evaporation of water is found to be greatly retarded by the supernatant crust of pyramidal crystals of sodium chloride that form if impure water, such as river water, is used for making up the brine. The rate of evaporation is very rapid, however, if distilled water is used since the surface remains free from crust.[35]

Boiling Point and Boiling Point Elevation.

In the original Treatise,[36] the boiling point of pure sodium chloride was stated to be 1490°C.: the value now accepted is 1413°C.[1,37–40]

A satisfactory formula for calculating the elevation of boiling point, ΔT_1, of saturated sodium chloride solutions at pressures ranging from 0·04 to 0·80 atmospheres is:[41]

$$\frac{\Delta T_0}{\Delta T_1} = \frac{T_0^2 C_0 L_1}{T_1^2 C_1 L_0}$$

where ΔT_0 is the elevation at unit atmosphere pressure, T_0 and T_1 are the boiling points of the pure solvent at one atmosphere pressure and the given pressure respectively, C_0 and C_1 the concentrations of the salt, and L_0 and L_1 the corresponding latent heats of vaporization. In estimating the boiling points of sodium chloride solutions, especially 'technical solutions', frequent use is made[42,43] of the Ramsey–Young rule and also Dühring's rule which states that if T_A and T'_A are the boiling points of a solution of a particular substance at pressures p and p', and T_B and T'_B the boiling points of a solution of another, chemically similar substance, at the same pressures p and p', then

$$\frac{(T'_A - T_A)}{(T'_B - T_B)} = \text{constant}$$

In this way, the boiling points of 'technical' sodium chloride solutions were obtained from data on potassium hydroxide solutions.[42]

A simple semiempirical equation has been used for calculating the boiling points of sodium chloride solutions from data on the decrease of vapour pressure.[44] But accurate ebulliometric measurements have been carried out on alkali halide solutions up to 4 molal, as well as on solutions of the halides containing arsenious oxide.[45] In the case of mixed sodium chloride–arsenious oxide solutions, the boiling point elevation can be additively computed within the limits of experimental error.[45]

When the concentration of a solution containing two salts is increased as boiling is continued, the solution gradually becomes saturated and a small quantity of solid salt appears. The temperature at which the appearance of the salt occurs is called the 'salt temperature', and it has been determined for a number of salt mixtures including aqueous mixtures of sodium chloride and potassium chloride and sodium chloride and sodium bromide. These data have been published graphically, and the relation between 'salt temperatures' and the two salts in the solution has been discussed.[46] For an aqueous solution of sodium chloride the 'salt temperature' is 108·7°C., and for aqueous potassium chloride it is 108·5°C.[46] In a mixed aqueous solution of these two salts the 'salt temperature' is higher than either of the above temperatures. When the composition of the solid separating out is 41·5 NaCl : 58·5 KCl the salt temperature is maximal at 112°C.[46]

Freezing Point and Freezing Point Depression.

The best representative value for the melting point of sodium chloride is 804°C.[1,36-38]

It is possible to calculate the depression of freezing point of sodium chloride solutions, with good accuracy at low concentrations, from the activity coefficients of the solvents. Rolla and Mariani[47,48] have discussed the relationships proposed by Bonino and Schottsky between activity coefficients and freezing point depressions, and have also calculated depressions for fairly concentrated solutions which conform closely to the experimental values; e.g. for a 0·00512 M. solution the calculated depression is 0·0192°C. and the experimental value is 0·0186°C. At the highest concentration studied, 1·2774 M., the calculated and experimental depressions are 4·3970 and 4·3457 respectively.[47]

The plot of depression of freezing point versus concentration for aqueous solutions of strong electrolytes usually becomes more and more curved as the concentration decreases so that extrapolation to zero concentration gives indefinite results. If a solution of potassium nitrate of constant concentration, instead of water, is used as solvent the plot becomes linear.[49] There is, however, no simple relation between the depression at zero concentration for electrolytes such as sodium chloride and most other alkali halides and the depression at zero concentration for a non-electrolyte such as urea.[49]

For aqueous solutions of a mixture of sodium chloride and ammonium chloride in which the range of total concentration is 1·5 to 2 M., the freezing point depression is practically constant at constant 'ionic strength', S. The latter is defined by $S = \Sigma y Z_i^2$, where $y = N_i/N_0$, the thermodynamic concentration, N_i and N_0 being the numbers of moles of solute and solvent respectively, and Z_i is the valency of the ion.[50] For solutions of sodium chloride mixed with dioxan in various ratios up to a total concentration of 2 M., the freezing points and osmatic coefficients of the salt have been determined.[51] Scatchard and Benedict[51] found that for aqueous dioxan solutions of NaCl, KCl and LiCl the osmatic coefficient ϕ, which is related to the depression of freezing point θ by

$$\phi = \frac{\theta}{1{\cdot}858\ \text{M.}}\left(1 + \frac{\theta}{1858}\right),$$

may be described generally by the following equation:

$$\phi = 1 + 0{\cdot}5\ A_1 x_1^{3/2} M^{1/2} + (B_{11}x_1^2 + 2B_{12}x_1x_2 + B_{22}x_2^2)\,M + 1{\cdot}5\ (C_{11}x_1^{5/2} + 2C_{12}x_1^{3/2}x_2)\,M^{3/2} + 2(D_{111}x_1^3 + 3D_{112}x_1^2x_2 + 3D_{122}x_1x_2^2 + D_{222}x_2^3)\,M^2 + 2{\cdot}5(E_{111}x_1^{7/2} + 3E_{112}x_1^{5/2}x_2 + 3E_{122}x_1^{3/2}x_2^2)\,M^{5/2}.$$

In this equation $M = m_1 + m_2$ where $m^{1/2}$ is the no. of moles of salt, $x_1 = m_1/M$ and $x_2 = m_2/M$. For all three salts $A_1 = 0{\cdot}52864$, $B_{22} = +0{\cdot}00534$, $D_{222} = +0{\cdot}00013$, $C_{12} = -0{\cdot}032$ and the other constants for sodium chloride are:

B_{11}	+0·38628
B_{12}	+0·07330
C_{11}	−0·24194
D_{111}	+0·09600
D_{112}	+0·01732
D_{122}	+0·00483
E_{111}	−0·01603
E_{112}	−0·00471
E_{122}	−0·00506

A freezing mixture with an equilibrium temperature of −18°C. can be made by mixing crushed ice, two parts, with one part of solid sodium chloride.[37]

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Gaseous Sodium Chloride

It has long been known[1] that the vapours of sodium and potassium chlorides at low pressures are ionized. One determination[2] of the ionization constant of sodium chloride at its boiling point gave a value of 4×10^{-13}. It is also known that a dimer of sodium chloride exists in the vapour phase. The binding energy of this gaseous dimer has been studied, and for the reaction: $2NaCl \rightleftharpoons (NaCl)_2$ at $0°$ K., $\Delta U = -1{\cdot}86$ *e.*V.[3]

An electron diffraction study[4] of the alkali metal halides has shown that the interatomic distances for sodium, potassium and rubidium halides in the molecules are approximately 10% less than the corresponding distances in the crystal lattices. The equilibrium internuclear separation for the sodium chloride molecule is, in fact, 2·51 A., and its heat of dissociation measured from the ground state - zero vibrational quantum number - to the onset of dissociation is 4·25 *e.*V.[6] The fundamental vibration frequency of this molecule is 380 $cm.^{-1}$.[6]

The formation of gaseous sodium chloride played a dominant part in the

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study of the interaction of alkali metal vapour with halogens carried out by Polanyi *et al.*[5] It appears that every collision of gaseous molecules of chlorine with gaseous sodium atoms leads to chemical change according to the equation: $Na + Cl_2 \rightleftharpoons NaCl + Cl$. The following reaction also occurs to a certain extent: $Na_2 + Cl \rightleftharpoons NaCl + Na$; the NaCl molecules so formed are activated and on collision with sodium atoms emit light. This work has been succinctly summarized.[7,8]

The migration of sodium chloride in the gas phase has been discussed elsewhere (see page 850).

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Absorption of High Energy Radiation by Sodium Chloride

The transparency of rock salt (free from potassium) to cosmic radiation has been measured[1] using a modified form of Kolhörster electrometer. The coefficient of mass absorption is $0{\cdot}7 \times 10^{-3}$ g.$^{-1}$cm.^{2}, which is well below the value of the coefficient of absorption of water for γ-radiation emitted by radium *C*.[2]

The transmission of electrons with kinetic energies in the range 0–12 *e.*V. through a thin layer of sodium chloride crystals evaporated on to a metal support has also been studied.[3]

Transmission of Sound Waves by Sodium Chloride

The velocity of sound in solid sodium chloride is $3{\cdot}32 \times 10^5$ cm. sec.$^{-1}$.[4]

Measurements of the velocity[5-8] and absorption[9-12] of ordinary and ultrasonic waves in sodium chloride solutions have not only given accurate values of the compressibility but have also helped to elucidate the structure of the electrolyte solution and the nature of ion-solvent interaction. The principles of the technique of ultrasonics and their electrochemical applications have been discussed.[13,14]

In a 10% aqueous solution of the salt at 20°C. the velocity of sound is $16{\cdot}005 \times 10^5$ cm. sec.$^{-1}$, and Table XV shows how the velocity varies with temperature for a 26% sodium chloride solution.[6]

TABLE XV.- THE VELOCITY OF SOUND IN 26% AQUEOUS SODIUM CHLORIDE SOLUTION

Temp. °C.	Velocity (10^5 cm.sec.$^{-1}$)	Density (g.c.c.$^{-1}$)
20	17·96	1·1972
25	17·99	1·1944
30	18·01	1·1917
40	18·02	1·1861

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Refractive Index

Solid Sodium Chloride.

The refractive indices at 18°C. of natural and synthetic sodium chloride crystals, given for the mean of the sodium doublet, 5893 A., are accepted to be 1·5443 and 1·5498 respectively.[1] Synthetic crystals prepared by inserting a seed into a cooling melt have, however, been obtained having a refractive index of 1·54430 ± 0·00004 at 5876 A., and 1·54055 and 1·55327 at 6563 A. and 4861 A., respectively, showing only slight deviations from the values for rock salt.[2]

Theoretical work based on light dispersion data[3] and the Schrödinger wave equation[4] have enabled the molecular refractivity of sodium chloride to be calculated with reasonable accuracy. Further details of several equations relating refractive index to other physical properties have been comprehensively treated by Partington.[5] The constants of one of these equations, that of Hartmann, have been determined for sodium chloride as well as for other alkali halides.[6] Yurev and Tonin[7] have calculated the refractive index of sodium chloride at 20°C. for wave-lengths from 0·589 to 17·68 μ using published data on temperature coefficients and refractive indices at other temperatures.

Aqueous Solutions of Sodium Chloride.

At a given temperature and for a fixed wave-length, aqueous solutions of many salts obey the equation $n - n_0 = a(1 - e^{-bC})$ where n and n_0 are the refractive indices for the solution and pure water respectively, C is the concentration in moles l.$^{-1}$ and a and b are constants characteristic of the salt: a depends on, but b is independent of, the wave-length. For a wave-length of 5893 A., and at 15°C., the constants a and b, for sodium chloride solutions are 0·22106 and 0·04478 respectively.[8]

Several workers have determined the refractive indices and equivalent and molecular refractivities of sodium chloride solutions over various wave-length and concentration ranges,[9-12] and in particular Kruis[13] has measured the relative refractive indices of sodium chloride solutions at 25°C. for fifteen wave-lengths between 4358 and 6678 A. with a precision of $\pm 3 \times 10^{5}$ These results, and the dependence of equivalent refractivity on concentration, have been tabulated and presented graphically. Below a concentration of 1 N., the equivalent refractivity deviates from the linear relation displayed by concentrated solutions, and it is conceivable that this is due to the lowering of the refraction of water caused by the presence of the sodium and chloride ions which disturb either the quasi-crystalline structure or the degree of polymerization of the solvent.[13] It is very difficult to obtain the equivalent refractivity of sodium chloride at infinite dilution by extrapolating the data at higher concentrations, but the value at 18°C. for 5893 A. is[14] 9·05. The refractive index of a 0·25 N. solution of sodium chloride is maximal at –3·5 ± 0·2°C., whereas for a 0·5 N. solution[15] it is maximal at –8·6 ± 1·2°C.

Accurate data on the refractive indices of mixtures of sodium chloride and potassium chloride solutions have been compiled.[16] Formulae are available which permit the calculation of the refractive indices of aqueous solutions of two mixed salts having a common ion, and the calculated values for the sodium chloride–potassium chloride solutions differ from the measured values by less than 0·00007.[17] The refractive indices of the system: sodium chloride-potassium chloride–ammonium chloride–water at 15°C. have been studied.[18]

Light Transmission and Light Scattering

The transparency and power of reflection of solid sodium chloride have frequently been studied because of their importance in experimental work in the infra-red.[19–25] Data are available for the absorption coefficients in the wave-length ranges 20–40 μ,[20] 40–75 μ[22] and 70–125 μ.[23] The results obtained using evaporated films of the order of 1 μ in thickness concur with those obtained for thin laminae cut from the crystal, the principal characteristic frequencies being at 61·1 μ and 51 μ.[22] The transmissions of thin films of sodium chloride evaporated in air at a pressure of 3 to 5 mm.Hg on to a sheet of nitrocellulose have been shown in graphical form for wave-lengths from 0·8 to 11 μ.[26] Thin plates of sodium chloride of about 8 μ in thickness, cut from rock salt, exhibit a maximum of reflection at 52 μ and a subsidiary peak at 39 μ.[27]

In the ultra-violet region, 190 to 1500 A., a film of sodium chloride distilled directly on to a ruled concave grating showed maximum absorptions at 350, 535, 655 and 890 A.[28] In the region 1990 to 2300 A., a comparison has been drawn between the absorption spectra of rock salt, of an aqueous solution of rock salt and of an aqueous solution of pure sodium chloride.[29] The rock salt is much more transparent than its aqueous solution and shows no temperature effect, whilst the solution of pure sodium chloride resembles rock salt rather than an aqueous solution of rock salt. Pure sodium chloride in glycerol (1·2 M.) at 20°C. has an optical density in the region 2170 to 2455 A. which is roughly nine times that of a similar water solution.[29] The optical densities of solutions of equal concentration (3 N.) with respect to chloride ion of sodium chloride and six other chlorides for the range 2170 to 2500 A. and from 20 to 80°C. have been tabulated.[30]

Recently much interest has been focused on the scattering of visible light by synthetic and natural sodium chloride single crystals.[31–35] It has been found that the total intensity of light scattered at an angle of 90° as a function of wave-length (from 2500 to 6600 A.) is forty times greater than that expected from thermal theory, and that the wave-length function does not vary inversely as the fourth power.[35] Moreover, only a small part of the scattering can be attributed to thermal fluctuations and the bulk has been attributed to a submicroscopic block structure. The estimated linear dimension of the blocks is of the order of 1500 A., and it appears that they constitute an intrinsic feature of the real structure of single crystals.[35]

Raman Spectrum

The Raman spectrum of rock salt, which has been obtained by irradiating a prism of the material with the resonance line of mercury, 2537 A., absorbing the unmodified scattered frequency with mercury vapour, and photographing the residual light, differs from that ordinarily observed for crystals in being very weak and having a continuous character.[36–39] A qualitative theory for this spectrum has been proposed by Fermi and Rasetti[36] and also by Blackman.[38]

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Luminescence of Sodium Chloride

Since Mellor wrote his original Treatise and referred particularly to the crystalloluminescence of sodium chloride (Mellor,II,531) the study of luminescence has made significant advances. This has been due in part to the detailed study of single crystals of alkali halides with and without small quantities of 'activators' - added materials which improve the luminescence. Sodium chloride is not one of the small group of substances which luminesce in the pure state.[1] The definition of 'pure state' with respect to luminescent materials is rather specific. The above statement really means that after repeated purification, until spectroscopic analysis shows the absence of foreign elements, sodium chloride loses its ability to luminesce. Nevertheless, it has been established[2] that sodium chloride from which all foreign material has been removed can be made to luminesce under certain conditions. If it is excited by absorption of powerful electromagnetic radiation (γ-rays, X-rays or ultra-violet light), the luminescence it displays is called photoluminescence; if it is exposed to electron bombardment the luminescence thus induced is cathodoluminescence and the light-emission produced by mechanical strain is triboluminescence.[1] In the discussion below, no precise meaning attaches to the separation of the terms fluorescence and phosphorescence. Generally, fluorescence refers to light emission which ceases within 10^{-8}sec. of the cessation of the excitation; phosphorescence refers to the emission of light for longer times after excitation ceases.[1]

Rock salt and synthetic sodium chloride which contain colour centres e.g. U-centres (see page 810), and also transparent rock salt which has been subject to irradiation by X-rays fluoresce and phosphoresce when excited by ultra-violet light.[2-22] This occurs with both single crystals and polycrystalline specimens.[1] The factual data recorded up to the mid-nineteen-forties, and their interpretation, have been summarized by Bose,[23] and more recent work by Garlick[1] and Kats.[24]

The luminescence of the ultra-violet excited X-rayed sodium chloride occurs both in the visible and in the ultra-violet regions of the spectrum.[2,4,6] The chief part of the ultra-violet phosphorescence lies below 1900 A., and a second zone lies between 1900 and 2500 A.[6,16] In the visible region, fluorescence wave-length maxima occur at 4700 and 5300 A.[9] The phosphorescence bands broaden and their maxima shift significantly with increasing temperature, e.g. the second ultra-violet zone maximum was observed by Podashevskii and Polonskii[7] to move from 2440 A. at –180°C. to 2490 A. at 15°C. and to 2520 A. at 100°C.

If the crystal is plastically deformed before excitation with ultra-violet light then in addition to the phosphorescence peak in the ultra-violet region 2350 A.,[16,25] another peak appears at 2950 A.[25] One investigator[26] has reported three phosphorescence peaks - at 2940, 2800 and 2370 A. - in the spectrum of plastically deformed natural rock salt. Moreover, a visible fluorescence peak at 4900 A., as well as the 4700 A. peak shown by a tempered crystal, appears when the crystal is plastically deformed.[25,27,28] This triboluminescence is quite reproducible.[29-31]

Sodium chloride containing a very small percentage of thallium as activator exhibits interesting luminescence characteristics. In the first place, three new absorption bands appear,[1] with wave-length maxima having photon energies corresponding to 4·87, 5·8 and 6·2 e.V.[1] Since these values differ but slightly from those observed when thallium ions are introduced into potassium chloride, rubidium chloride and caesium chloride the view that they are characteristic of the thallium centres is substantiated.[1] Secondly, as for pure sodium chloride containing colour centres, thallium-activated sodium chloride has a luminescence emission consisting of broad bands situated in the near ultra-violet and visible regions.[1,31-33] These bands are excited with the same relative intensities whether absorption takes place in any of the three absorption bands, the photon energies of the wave-length maxima of which have been given above.[1] Thirdly, if the concentration of the thallium is below 0·0015 mol.% only fluorescence is detectable, but at higher concentration a slowly decaying phosphorescence occurs having the same emission spectrum as the fluorescence.[1] The decay rate of this ultra-violet excited phosphorescence is of exponential form, and it increases exponentially with increasing temperature. Equations (1) and (2) summarize these statements:

$$I = I_0 \exp(-at) \qquad \text{............(1)}$$

and

$$a = s \exp(-E/kT) \qquad \text{.........(2)}$$

where I_0 and I are the intensity of phosphorescence at the beginning of the decay and after a time t respectively, a is a constant having the same dimensions as frequency, k is the Boltzmann constant, T the absolute temperature and the values of the constants E and s are 0·67 e.V. and $2{\cdot}9 \times 10^9$sec.$^{-1}$ respectively.[1] Another feature of the thallium-activated sodium chloride phosphor is that the ratio of the phosphorescence light output to the absorption is approximately proportional to the thallium concentration. Since the absorption is also proportional to the thallium concentration, the light output of phosphorescence is proportional to the square of the activator concentration.[1] All these properties are explicable in terms of the modern theory of luminescence,[34] according to which phosphorescence involves the excitation of electrons to metastable states or traps where they are held temporarily, and whence they escape gradually by thermal excitation.

Although the phosphorescence of sodium chloride containing small amounts of silver has been known for almost thirty years,[35] it was not until the development of nuclear science and of the concomitant need for methods of detecting high-energy radiation that this phenomenon received detailed attention. Since 1950, many studies of the luminescence and light-storage properties of sodium chloride containing about 1% of silver chloride or metallic silver have been made.[36-43] Parfianovich,[38] who introduced metallic silver into the sodium chloride lattice by electrolysis at about 700°C. and excited the luminescence spectrum by X-rays, observed the position of the maximum of the broad luminescence band at room temperature at about 4400 A. By conducting excitation at very low temperatures and measuring the thermoluminescence accompanying the gradual heating to a few hundred degrees Centigrade, he estimated the depth below the conduction band of the level at which electrons are fixed at room temperature as about 0·74 e.V.[38,39] Kats,[41] using a single mixed crystal of sodium chloride and silver chloride grown from the melt, found that, after X-irradiation followed by excitation with ultra-violet light, a bright orange fluorescence occurs, the maximum wave-length being 6300 A. This maximum shifts to shorter wave-length on heating to 200° to 250°C. as evidenced by the yellowish green fluorescence.[41] Two bands with maxima at 2750 and 3400 A. occur in the excitation spectrum which itself extends from 2400 to 3800 A., and the 2750 A. wave-length excites the yellowish green, and the 3400 A. the orange fluorescence.[41] In agreement with Parfianovich,[39] Kats[41] observed phosphorescence with maxima at about 4500 and 2480 A.: he also adduced evidence to show that the blue and ultra-violet luminescence are due to silver ions, and the orange and yellowish green emission to silver atoms.

A few papers dealing with the luminescence of sodium chloride containing other foreign species are available. Luminescence bands of salt crystals containing metallic copper, nickel and palladium appear at 3600, 6250 and 3250 A. respectively following excitation by X-rays.[38,39,39a] Crystals containing manganese[44] emit fluorescence in the visible region during exposure to ultra-violet light, but luminescence of sodium chloride–lead phosphors is rather complex.[45] Melt-grown specimens of the latter display an asymmetrical absorption band with a peak wave-length at 2730 A.[45] The variation of the emission spectrum with excitation wave-length within this band shows that it consists of two poorly resolved absorption bands having peaks - one at 2900 as well as that at 2730 A. Irradiation in the band of maximum 2730 A., with low lead concentration, produces an emission in the near ultra-violet region, the maximum occurring at a wave-length of 3200 A. Irradiation in the other band, also at low lead concentration, produces a visible emission, the maximum occurring at 4500 A.[45] At high lead concentrations, irradiation in the band of maximum 2730 A. produces, in addition to the 3200 A.-peaked band, a second near ultra-violet emission band the peak of which occurs at 3850 A.[45] Sodium chloride–lead phosphors are unstable and deteriorate, after a few days at room temperature and more rapidly at 130°C.,[45] and all the above-mentioned

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absorptions and emissions are destroyed if the phosphor is irradiated with *X*-rays.[45]

Neither manganese nor lead activates red fluorescence in synthetic or natural sodium chloride[46] - the presence of both is necessary.[46-48] The phosphorescence phenomena of phosphors composed of sodium chloride, potassium chloride and thallous nitrate,[49] and sodium chloride, zinc sulphide and samarium[50] have been studied.

Crystalloluminescence.

When sodium chloride is crystallized by adding hydrochloric acid to, or by freezing, an aqueous solution of the salt ultra-violet light is emitted.[51-57] The characteristics of this luminescence for various conditions of precipitation by hydrochloric acid, which produces a greater effect than straightforward freezing, have been studied in detail by Racz.[52-57] The luminescence takes place in two steps. First comes an intense continuous glow of short duration reaching a maximum intensity after 10 to 20 sec.; this is often termed, in this context, the 'fluorescence' part of the phenomenon. The second step, known as the 'phosphorescence', attains a maximum about 2 min. later and decreases exponentially with time.[57] The ratio of the intensity of the 'phosphorescence' to that of the 'fluorescence' is always less than unity, but the total phosphorescent emission is several times greater than the fluorescent emission.[57] Both 'fluorescence' and 'phosphorescence', however, have the same spectrum, the wave-length maximum being in the vicinity of 2400 A.[55,56] Other relevant features of the crystalloluminescence are that the intensity of emission is diminished by agitation of the solution, by rise of temperature, and by the addition of an aged sodium chloride crystal[53,56] (a freshly precipitated crystal enhances the effect).[56] Kinetic study shows that the entire process has an induction period which varies with the acid concentration, being as high as 40 sec. with dilute hydrochloric acid.[57]

Racz[52-57] has developed a theory which accounts qualitatively for some of the foregoing facts. It is based on the principle that crystals grow not by the simple deposition of an ion from solution on to the lattice, but as a result of the formation of a 'seed' or a nucleus. Calculations show that the energy produced in the course of normal growth is inadequate to account for the energy emitted in crystalloluminescence. Special processes are necessary for the liberation of photons of wave-length 2400 A. on precipitation of sodium chloride. This, coupled with the fact that only one photon is emitted per 10^{10} molecules precipitated, led to the proposition that during the development of the crystal two linear 'seeds' can meet, or an ion can insert itself between the ends of the two rows of ions.[56] The energy liberated by such processes would be of satisfactory magnitude.

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Photoconductance and Related Phenomena

Studies of the photoconductance of sodium chloride have not only confirmed the physical and theoretical models of the various point defects that can occur in alkali halides (see 'Colour Centres'), but have also produced qualitative and quantitative information about the electronic energy levels of the crystal lattice.[1-3]

Ordinary transparent sodium chloride, when illuminated with radiation of

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wave-lengths greater than 1280 A., shows no sign of photoconductance.[4,5] (For sodium chloride, 1280 A. corresponds to the position of the limit of the stationary states of an electron bound to a positive hole, and it is in fact the position of the peak of the second ultra-violet band of the crystal[6] (see page 804)). When sodium chloride absorbs a quantum of radiation of frequency greater than that of this series limit a free electron and a free positive hole should be produced. Illumination with radiation of wave-lengths less than 1280 A. should therefore give rise to photoconductance. Although there is clear evidence that photoconductance at room temperature rises significantly at this absorption peak,[5] the situation is not as simple as the above mechanism would suggest. For example, at low temperatures, photoconductance is not observed at all.[6] From these facts it is concluded that an electron and a positive hole are not separated directly by the light, but that this process can be facilitated by the thermal energy of the surrounding atoms.

Whereas pure, transparent sodium chloride or rock salt does not display photoconductance to any appreciable extent, samples containing *F*-centres do. Now that the methods of producing colour centres are well understood (see page 804), the apparently confusing effects observed by early investigators can be appreciated. Thus, Roentgen[7] in 1921 found that exposure of sodium chloride crystals to sunlight or ultra-violet light did not influence the electrical conductance, but that short exposure first of all to *X*-rays or γ-rays followed by sunlight or ultra-violet light caused the conductance to increase 40,000 times. Shortly afterwards, Gyulai[8,9] discovered that sodium chloride crystals which had been coloured yellow by exposure to *X*-rays showed electrical conductance when exposed to light in the wave-length range 254 to 680 mμ, the maximum response being obtained at 470 mμ. Smekal[10] and Podashewskii[11-13] noted that plastic deformation of yellow sodium chloride caused decolouration which was also accompanied by a decrease in the photoconductance. The work of Pohl[14] and others[15-19] amply confirmed these facts. It is now known[20] that the significant factors are that: (*a*) irradiation by *X*-rays produces colour centres· (*b*) the peak of the *F*-band is at 470 mμ; and (*c*) plastic deformation can seriously affect the colour centre concentration through the generation and precipitation of lattice vacancies at dislocations. Other important considerations as to photoconductance which were ultimately recognized by the earlier workers were the distinction between primary and secondary photoelectric current[6,21] and the influence of space-charge.[22,23] The motion in an applied electric field of the electrons which have been raised to the conduction band of the crystal from lower bands as a result of illumination, together with any motion of the positive holes created simultaneously, constitutes the primary photoelectric current. So long as only this primary current is flowing, no net flow of electrons should enter the crystal from the cathode. Under certain conditions, however, the continued passage of the primary current facilitates the transfer of electrons from the cathode to the juxtaposed crystal, thus giving rise to the secondary photoelectric current. In this discussion, photoconductance refers to the primary current only, unless the contrary is stated. The space-charge is set up in the crystal because positive holes which are released by the light, unlike liberated electrons, do not move.[6] The electrical field within the crystal is therefore disturbed and very often, after prolonged illumination, the actual magnitude of the electric field falls to a small fraction of that originally applied.

While most of the early work on the photoconductance of sodium chloride was carried out using crystals which had been irradiated with *X*-rays beforehand, it has been the practice in recent years to use samples into which excess sodium has been incorporated from the vapour phase or by electrolysis.[6,20,24,25] Fig. 1 shows the results for the additively coloured salt, after it had been illuminated for 5 sec. with visible blue light of wave-length 470 mμ (*i.e.* in the *F*-band) and 12 sec. later by infra-red light of wave-length

700 mμ at each of four different temperatures.[6]

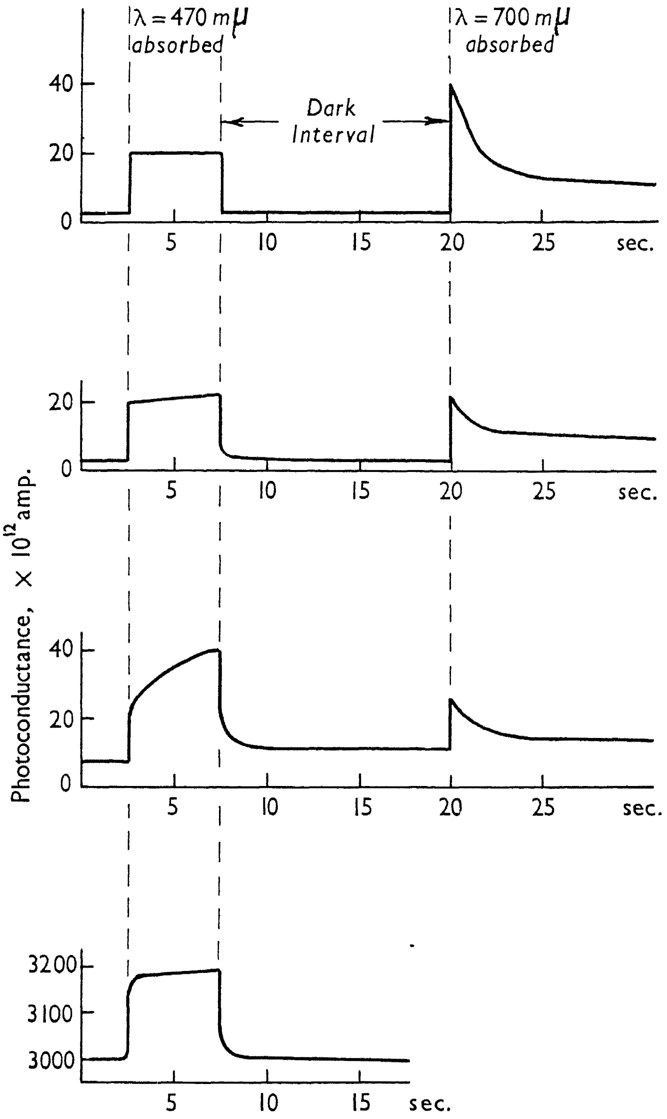

FIG. 1. PHOTOCONDUCTANCE IN SODIUM CHLORIDE AS A FUNCTION OF TIME, THE CRYSTAL BEING ILLUMINATED FIRST WITH BLUE AND THEN WITH RED LIGHT

At the lowest temperature, illumination in the F-band gave a current which stopped and started instantaneously with the light, and the total current was proportional to the light intensity.[6,26] To be precise, less than 5×10^{-6}sec. is required to initiate photoconductance in sodium chloride crystals.[26] It follows that the mean range or *Schubweg*,[6,20] which is defined as the effective distance a liberated electron will travel in the direction of the applied electric field before it is trapped (e.g. by an *F*-centre), is independent of the number of electrons ejected. Since current continues after the cessation of illumination at higher temperatures, it follows that the trapped electrons are not stable at these temperatures. Infra-red radiation, as shown in Fig. 1, assists the escape of trapped electrons.

When specimens of sodium chloride containing varying concentrations of *F*-centres are studied it is found that the *Schubweg* is inversely proportional to the *F*-centre concentration.[6] This supports the belief[6,20] that trapping of electrons occurs at *F*-centres thereby producing *F'* centres (see page 808).

The interpretation of Fig. 2,[6,27,28] which shows how the photoconductance varies with temperature for sodium chloride containing 10^{16} colour centres per cm.[3] when irradiated with light of wave-length 470 mμ, has been given.[1,6,15]

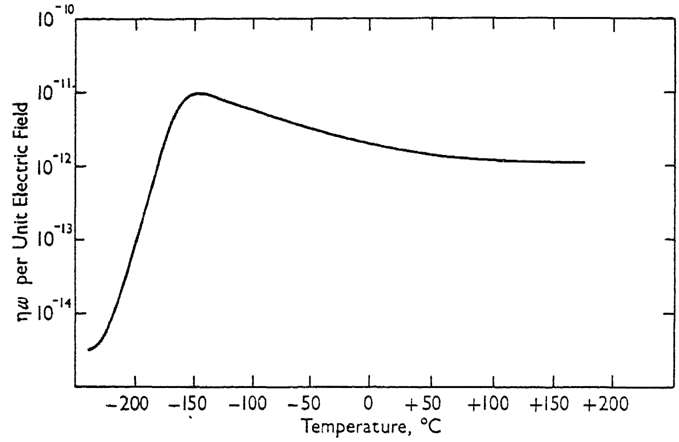

FIG. 2.[6] PHOTOCONDUCTANCE-TEMPERATURE CURVE FOR SODIUM CHLORIDE CONTAINING 10^{16} COLOUR CENTRES (IRRADIATED WITH $\lambda = 470$mμ)

η is the quantum efficiency for freeing the photoelectron and ω is the mean range or *Schubweg*. The sharp drop in $\eta\omega$ at −150°C. is thought to be due to a drop in η. A similar drop in the quantum efficiency of the $F \rightarrow F'$ transformation occurs in the absence of an electric field at the same temperature.[6] Mott and Gurney[6] have been able to account quantitatively for the shape of this curve, which can be fitted fairly well to the formula:-

$$\eta = \frac{1}{1 + p\exp\left(\frac{E}{kT}\right)}$$

with $p = 0{\cdot}0033$ and $E \approx 0{\cdot}075$ e.V.

The same authors[6] have given an elegant explanation of the secondary photoelectric current in sodium chloride which appears after the primary current has been flowing for a certain time. It was observed that when sodium chloride crystals containing *F*-centres, due to stoicheiometric excess of sodium, were illuminated in the *F*-band a small, steady current was produced: this was not reduced at all by any space-charge, but it occurred only when the whole of the crystal was illuminated.[29]

It has also been shown[6] that the photoconductance observed with crystals of blue sodium chloride,[24,30] which are known to contain colloidal sodium (see page 804), is due to the ejection of electrons from the particles of the colloidally dispersed metal.

The techniques that have been devised for measuring the Hall effect in photoconducting sodium chloride at low temperatures yield data on the electronic mobility and the capture cross-section of *F*-centres for electrons.[31-33] The electronic mobility measured at 84°K. is 250 ± 50 sq. cm. $v.^{-1}$sec.$^{-1}$, this decreases to 25 ± 25 sq. cm. $v.^{-1}$ sec.$^{-1}$ at 200°K. At 200°K. also, the capture cross-section is of the order of 1×10^{-15} sq. cm.[31]

Secondary Electron Emission and Field Emission.

Secondary electron emission is quite distinct from the secondary photoelectric current referred to above. It is the electron emission induced by electron bombardment. This subject is still in its infancy, especially in regard to theoretical development, and but few papers on the secondary emission of sodium chloride are available.[34-36] Wright[35] found that sodium chloride, when bombarded with slow electrons, has a secondary emission threshold at 10 e.V. The results of some earlier investigations, quoted by Dekkar[37] in a review of the phenomenon, show that, for an evaporated layer of sodium chloride, the maximum yield (*i.e.* the maximum number of electrons emitted per incident primary electron), in the low energy region, is 6·0. For single crystals of the salt cleaved in vacuum the maximum yield is approximately 8·0.[37] The radiation damage produced by the incident primary beam causes a reduction in the yield.[37]

Emission of electrons from an ionic crystal occurs when an intense electric field is applied between it and a suitable anode. This effect, for sodium chloride, has been studied by the technique of field emission microscopy[38,39] which provides a powerful means of exploring the solid surface, e.g. of determining the variation of work function with crystal plane and the movement of adsorbed species.

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Colour Centres

Pure sodium chloride is highly transparent in the wide range of wavelengths between the fundamental electronic absorption in the far ultra-violet (Fig. 3) and the absorption of the lattice vibration in the far infra-red (Fig. 4).

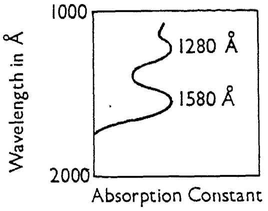


FIG. 3. ULTRA-VIOLET ABSORPTION OF SODIUM CHLORIDE[32]

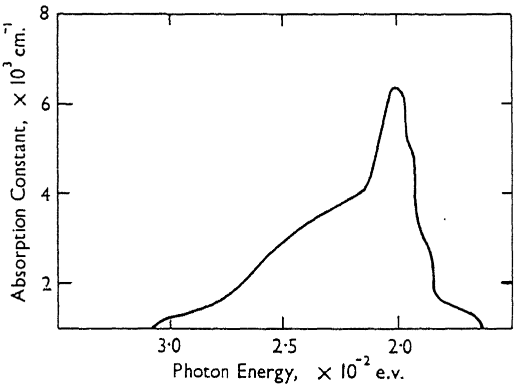


FIG. 4. INFRA-RED ABSORPTION OF THE LATTICE VIBRATIONS OF SODIUM CHLORIDE[32]

Rock salt, however, (Mellor,II,530) is either colourless or varies in colour from white to grey, to yellow, to reddish-yellow and often blue or purple.

Ever since Gouldstein[1] first observed the colouration of polar crystals by high energy radiation, a plethora of tentative explanations has been advanced for the occurrence of coloured rock salt. Some of the explanations propounded up to 1922, which were discussed by Mellor, were later found to contain an element of truth. Subsequent reviews,[2-6] dealing mainly with the painstaking researches of Przibram,[7-18] Gyulai[19,20] and other pioneers in this field,[21-30] are available; but these do not survey the results obtained by several schools of solid state physicists who, in recent years, have concentrated on the optical properties of alkali metal halides for the general study of crystalline imperfections.

At present an extensive collection of factual material appertaining to coloured sodium chloride is available, and some of the models and mechanisms that have been suggested to accommodate these facts have been vigorously tested. Recent reviews dealing comprehensively with coloured alkali halide crystals have been published by Seitz[31] and Pick.[32]

It is possible to colour sodium chloride in a number of ways. One of the simplest is to introduce a stoicheiometric excess of sodium, for example, by heating the crystal in sodium vapour to approximately 700°C. for several hours, in which time the metal diffuses from the vapour phase into the crystal, and then cooling rapidly.[33-37] The new absorption band has its maximum at 4650 A.[33] to 4700 A.,[31] corresponding to a photon energy of 2·7 e.V. Only when sodium chloride is treated in this way will it assume a yellow colour: if, instead of quenching, the crystal is cooled slowly down to room temperature then the effect of the sodium is to yield a blue-tinted product.[32]

Colouration of sodium chloride by electrolysis at elevated temperatures is also the result of non-stoicheiometry. If the oxidation of the sodium deposited at the cathode is prevented, e.g. by means of a vacuum tight contact between the crystal and the cathode, the sodium will diffuse into the lattice giving rise to non-stoicheiometry owing to the existence of chloride ion vacancies.[31,32,38]

Coloured sodium chloride may also be produced by the introduction of suitable chemical impurities, e.g. ferric ions, and other transition element ions having excited energy levels separated from the ground state by an optical frequency.[39-43] It is not, however, essential for the impurity ions to be themselves coloured. Thus the introduction of small quantities of the chlorides of strontium or barium, or the incorporation of small quantities of the metals lithium, potassium or rubidium into synthetic and natural sodium chloride can result in absorption in the visible region of the spectrum.[31,44-47] This phenomenon is further discussed below.

Another simple and powerful method of colouring sodium chloride is exposure to high energy radiation such as ultra-violet light,[48,49] *X*-rays,[31,32,50,51] γ-rays,[31,32,52-55] fast electrons,[52-64] α-particles and neutrons.[31,32] For a more exhaustive treatment of this phenomenon the reader is referred to the section, to be published in a later Supplement, on the effects of ionising radiation on the salts of the alkali metals. The absorption band produced in these ways has the same bell shape as that produced by excess sodium, but the maximum intensity is very much less.[49] If, however, the crystal has been deformed beforehand the maximum intensity is greater.[49,65-68] Colour that has been produced by γ-rays, *X*-rays and ultra-violet light is less stable than that produced by adding excess sodium, e.g. when a crystal coloured by *X*-rays is illuminated by light in any part of the absorption band it is completely bleached.[49,68,69] More is said below about the conditions under which bleaching occurs, but it should be noted here that sodium chloride that has been bombarded with fast electrons develops a colour which is more stable than that formed by *X*-rays or ultra-violet light, a fact which appears to be related to the release of chlorine from the lattice during bombardment leaving a stoicheiometric excess of sodium.[49] The colour is also rendered more stable if the sodium chloride is sensitized beforehand by the addition of small amounts of sodium hydride.[32]

Whenever sodium chloride develops colour it is said to contain colour centres, these being lattice defects which absorb light. The simplest type of colour centre is that produced by excess sodium or by irradiation.

This is known as the *F*-centre, the name being derived from the German 'Farbe'.[70] The absorption band produced by the absorbing *F*-centres is termed the *F*-band, and its wave-length maximum for sodium chloride is at 465 mμ, the half-width at 20°C. being 0.47 mμ.[32]

Many types of colour centres other than *F*-centres are known: several of these are produced simultaneously with the *F*-centres when these are generated by irradiation. For this reason, *F*-centres in sodium chloride have been more frequently studied when they have been produced by addition of excess sodium. Before proceeding to discuss the precise nature, and the various theoretical models, of *F*-centres, some of the more important characteristics of additively coloured sodium chloride will first of all be considered. In particular, the distinction between coloured sodium chloride arising from the presence of colloidal particles, and coloured sodium chloride arising from the occurrence of lattice defects is outlined.

At one stage in the history of this subject, the belief was prevalent that colour centres arose from the existence of small colloidal particles of excess metal dispersed in the lattice. Indeed, visual inspection with an ultramicroscope reveals the presence of colloidal particles in blue rock salt, which appears to vindicate such a conclusion.[71-78] Moreover, Gyulai[19] demonstrated that the blue colour observed in specimens of natural rock salt duplicates the blue colour obtained when yellow, additively coloured sodium chloride - which, by definition, contains *F*-centres - is annealed at temperatures in the region of 400°C., thereby proving that the colloidal particles are composed of sodium. It is now generally accepted that blue rock salt does in fact owe its colour to the presence of colloidally dispersed sodium, and that yellow sodium chloride (natural or synthetic) which exhibits the *F*-band is something quite distinct.[31] The ambiguity was partly removed by Savostyanova,[79,80] who calculated that the wave-length maximum of the light scattered by metallic spheres of sodium in sodium chloride occurs at longer wave-lengths (>5500 A.) than the maximum of the *F*-band, and partly by Mollwo,[81] who established this experimentally by examining the absorption bands in additively coloured crystals for various times of annealing. The colloid bands are shifted to longer wave-length with increased annealing in accordance with Savostyanova's calculations.[81-84] For example, the peak of the colloid band in additively coloured sodium chloride was observed to shift from 5700 to 6200 A. on heating from 300° to 450°C., but it could not be shifted beyond 6500 A.[81]

The investigations of Scott[85,86] and his school have added significantly to our knowledge of the colloid bands. Just as the *F*-band is attributed to the *F*-centre, so the colloid bands are attributed to colloid centres. The latter behave as if they constitute a monatomic vapour in equilibrium with a solid or liquid phase.[86] From the equilibrium density of *F*-centres, obtained by measuring the area of the *F*-band, and its variation with temperature it has been estimated that the energy required to form an *F*-centre from a colloid centre in sodium chloride is about 9.0 kg.-cal./mole, or about 0.39 e.V. per *F*-centre at 490°C.[86] Scott *et al.*[86] also found that the wave-length at the peak of the colloid band is 5650 A., that the total area under the *F*- and colloid bands is not constant, and that the colloid band vanishes at temperatures in the vicinity of 600°C.

When a stoicheiometric excess of sodium is introduced into an evaporated layer of sodium chloride both the colloid band and the *F*-band appear; the position of the latter is, however, displaced in the direction of shorter wave-lengths relative to the position in the normally coloured crystals[87,88] (Fig. 5). The third band in Fig. 5 occurring in the region of 720 mμ is the *M*-band discussed below.

Two other bands known as the α- and β-bands have recently been discovered[31,89] and are closely related to the *F*-band. Whenever a rock salt crystal

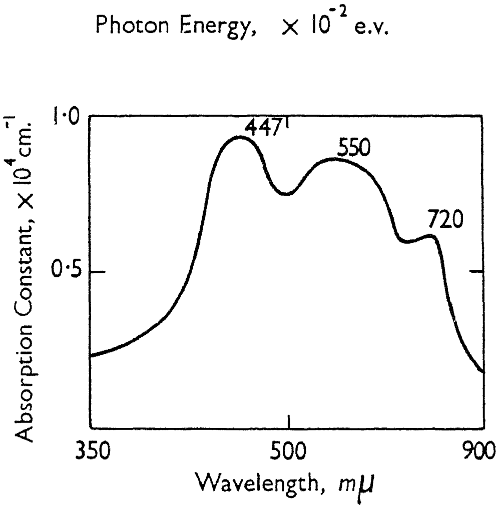


FIG. 5. ABSORPTION SPECTRUM OF EVAPORATED SODIUM CHLORIDE CONTAINING EXCESS SODIUM (LEFT TO RIGHT: *F*-BAND, COLLOID BAND AND *M*-BAND)

contains *F*-centres, introduced either additively or by irradiation, an absorption peak called the β-band appears just to the long wave side of the fundamental absorption band in the ultra-violet.[31,32,89] The β-band does not appear in the transparent crystal. If the *F*-band intensity is diminished, e.g. by bleaching with light in the *F*-band, the β-band diminishes in proportion to the diminution of the *F*-band and a new band, called the α-band, appears just to the long wave-length side of the β-band and grows in proportion to the decrease in the *F*-band. On heating, the α-band disappears and both the *F*-band and the β-band reappear with their original intensity.

Nature of the *F*-Centre.

de Boer[90] in 1937 formulated an atomistic model of the *F*-centre which can account for all the facts that have so far been observed. It is generally accepted that in additively coloured sodium chloride the sodium atoms fit into the lattice in normal sodium ion sites, a corresponding number of anion vacancies being created in the process. A negative ion vacancy, in this and in other lattices, behaves electrostatically as a positive charge so that an electron moving about such a vacancy resembles, qualitatively, a hydrogen atom. The *F*-centre is identified as an electron bound to an anion vacancy, the electron being provided by the ionization of an alkali atom on entering the lattice.[31,32,90] With *F*-centres generated by high energy radiation the precursory steps are the dissociation of a small number of alkali halide molecules and the production of atomically dispersed alkali. The equivalent quantity of free halogen also affects the absorption spectra (see page 809) Fig. 6 illustrates the *F*-centre point defect.

Na^+	Cl^-	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+
Na^+	$\boxed{e}$	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+
Na^+	Cl^-	Na^+	Cl^-

FIG. 6. *F*-CENTRE IN SODIUM CHLORIDE CONTAINING EXCESS SODIUM (*e* REPRESENTS AN ELECTRON)

The facts that support the de Boer model of the *F*-centre may be summarized as follows.

The *F*-band absorption is characteristic of sodium chloride and is unchanged if other alkali metal atoms are inserted instead of sodium as excess species.[44] Coloured rock salt and other alkali halide crystals are less dense than their colourless analogues,[31,32] but it should be remarked that this evidence alone is inconclusive as the decrease in density could conceivably be associated with electrons bound to interstitial alkali ions. Crystals with *F*-centres can be bleached by illumination with light absorbed in the *F*-band, and since illumination in any part of the band bleaches the whole of the band it follows that the *F*-centres, in any particular crystal, are all similar, the width of the band being attributable to the thermal vibration of the ions. The bleaching is believed to be due to the ionization of the *F*-centre, as it is accompanied by photoconductance (p. 799). The paramagnetic susceptibility of the *F*-centre corresponds closely to the contribution due to spin only of one electron.[91] The state of the *F*-centre electron, having as its nearest neighbours six cations, accounts for the width and shape of the electron spin resonance line.[92] Finally, many detailed theoretical calculations based on this model have all proved successful,[93-103] e.g. Pekar[32,101-103] calculated the half width of the sodium chloride *F*-band at 20°C. to be 0·47 mμ, and others[96] calculated the photon energy corresponding to the wave-length peak in the *F*-band to be 2·68 e.V., both in excellent agreement with the observed quantities.

Although the *F*-centre is the only colour centre bearing a trapped electron which has been clearly understood physically and theoretically, there is substantial evidence to indicate that other electron bearing centres exist. If rock salt already coloured by *F*-centres is irradiated at low temperatures with light of wave-length within the *F*-band, a broad band on the red side of the *F*-band is produced, and the intensity of the *F*-band is decreased to a corresponding extent.[32,104-106] The new band is called the *F′*-band. Under favourable conditions as many as 80% of the electrons in the *F* state may be transferred to the *F′* state. The process $F \rightarrow F'$ may be reversed by absorption of light in the wave-length range of the *F′*-band. And the significant facts emerge that with increasing temperature the quantum efficiency of the $F' \rightarrow F$ process falls smoothly from a maximum of two to less than one at a temperature in the region of −100°C., while the quantum efficiency of the $F \rightarrow F'$ process increases smoothly with increasing temperature to a maximum of two in the same low temperature range. Thus, one optical excitation results in the alteration of the state of two electrons, *i.e.* two *F*-centres are destroyed per *F′*-centre formed. It is therefore assumed that one *F*-centre is ionized by the incident radiation, and the liberated electron is then captured by another *F*-centre to form an *F′*-centre consisting of an anion vacancy with two attached electrons.[32] This conclusion is supported by the observation that the displacement range (the distance by which the free electron is displaced in unit field strength) of the photoelectrons is directly proportional to the concentration of the *F*-centres. Thus, Fig. 7 represents pictorially the nature of the *F′*-centre in sodium chloride.

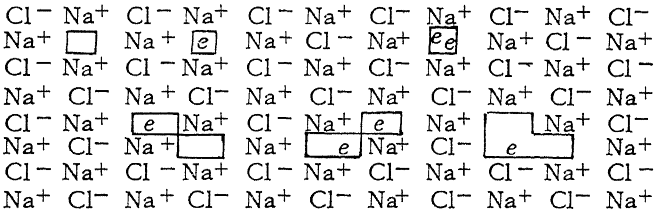
Na^+	Cl^-	Na^+	Cl^-
Cl^-	Na^+	$\boxed{{}^{e}e}$	Na^+
Na^+	Cl^-	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+
Na^+	Cl^-	Na^+	Cl^-

FIG. 7. *F′*-CENTRE IN SODIUM CHLORIDE

The electronic changes involved in the absorption of the α- and β-bands, whose relations to the *F*-band have already been outlined, are still open to question. Since both these imperfection-induced bands occur on the edge of the fundamental absorption band of the lattice, it may reasonably be assumed that they are associated with excitation of electrons on the halogen ions to well-defined higher energy levels not present in the perfect crystal.[31] It has been suggested[107] that the α-band arises from an electron transition between a halogen ion and the first level of a halogen vacancy, and that the β-band arises from the transition of an electron on the halogen ion to the second level of the *F*-centre.

The *K*-band, which occurs as a hump on the tail of the short wave-length side of the *F* band (absorption maximum at 290 mμ, subordinate maximum at 450 mμ for rock salt),[108,109] was at one time believed to be the result of excitations to the higher discrete levels of the *F*-centres.[107] The situation is, however, more complicated than this, and it appears possible that the *K*-band may be due to *F*-centres in the neighbourhood of lattice dislocations.[107,110] The *K*-band may be induced in rock salt by bombarding with electrons from a pointed cathode at temperatures below 420°C., or by irradiating at 570°C., quenching to below 450°C. and applying 300 V. between flat electrodes.[108]

The other electron-bearing colour centres which have been discovered are those that give rise to the *R*- and *M*-bands. When any alkali halide is irradiated at room temperature with light in the *F*-band, a series of bands appears on the long wave-length side of the *F*-band.[111-114] For sodium chloride the peak of the *M*-band has a photon energy of 1·72 e.V.[111] (see also Fig. 5.) In 1946, Seitz proposed the models shown in Fig. 8 for the *R*- and *M*-centres.[31] No work has yet appeared which contravenes this picture:[112-114] in fact, the calculations of Uemura *et al.*[109] lead to a value for the photon energy corresponding to the peaks in the *M*-band of 1·73 e.V., in very good agreement with the observed value.


Cl⁻ Na⁺ Cl⁻ Na⁺ Cl⁻ Na⁺ Cl⁻ Na⁺ Cl⁻ Na⁺ Cl⁻
Na⁺ □ Na⁺ e Na⁺ Cl⁻ Na⁺ ee Na⁺ Cl⁻ Na⁺
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Na⁺ Cl⁻ Na⁺ Na⁺ e Na⁺ Cl⁻ e Na⁺
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Na⁺ Cl⁻ Na⁺ Cl⁻ Na⁺ Cl⁻ Na⁺ Cl⁻ Na⁺ Cl⁻ Na⁺

FIG. 8. COLOUR CENTRES IN SODIUM CHLORIDE. FROM LEFT TO RIGHT, SECOND LINE: α-CENTRE (ANION VACANCY), *F*(β)-CENTRE AND *F*′-CENTRE. FIFTH AND SIXTH LINES: R_1-CENTRE, R_2-CENTRE AND *M*-CENTRE

Hole Centres.

Besides the single and aggregate centres discussed above, sodium chloride also contains hole centres. These absorb in the ultra-violet region of the spectrum and are therefore also called *V*-centres.[31,32] Hole centres and their associated bands can be produced very readily by exposing the crystals to *X*-rays or a beam of fast electrons, just as for *F*-centre production.[115-119] In fact, *V*-centres are created simultaneously with *F*-centres; and Pick[116] has shown that their concentration is roughly of the same order of magnitude as the concentration of the *F*-centres. The conclusion follows naturally that *V*-centres are the 'antimorphs' of the *F* type centres.[31] Accordingly, they should contain holes (*i.e.* halogen ions deprived of their electrons - in other words, free halogen atoms) instead of electrons. The hole will be attracted by a cation vacancy in the same way as an excess electron is attracted to an anion vacancy. Seitz[31] models for the various *V*-centres which give rise to the series of *V* bands at 3450, 2226 and 2100 A. are shown in Fig. 9. There is experimental support for these, but it has been stated[120] that they are rather speculative in that they are founded on the principle that a hole behaves like an excess electron, a statement which requires full justification. One investigation[121] on the nature of *V*-centres led to the view that V_1-centres arise from isolated holes, V_2-centres arise as a pair of holes associated with a cation vacancy, and V_3-centres arise from holes trapped at a cation vacancy. These conclusions also have been criticized.[31]

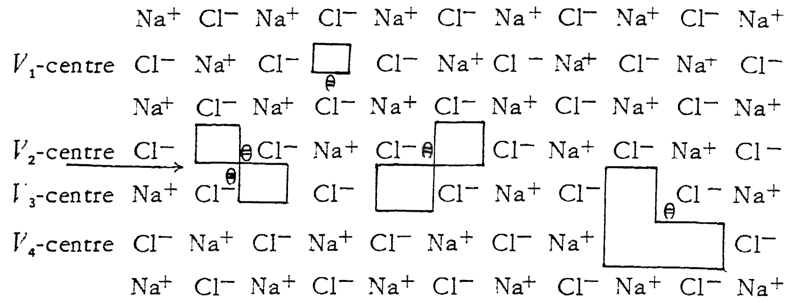
Na+ Cl− Na+ Cl− Na+ Cl− Na+ Cl− Na+ Cl− Na+
V_1-centre Cl− Na+ Cl− θ Cl− Na+ Cl − Na+ Cl− Na+ Cl−
Na+ Cl− Na+ Cl− Na+ Cl− Na+ Cl− Na+ Cl− Na+
V_2-centre Cl− θ Cl− Na+ Cl− θ Cl− Na+ Cl− Na+ Cl−
V_3-centre Na+ Cl− θ Cl− Cl− Na+ Cl− θ Cl− Na+
V_4-centre Cl− Na+ Cl− Na+ Cl− Na+ Cl− Na+ Cl−
Na+ Cl− Na+ Cl− Na+ Cl− Na+ Cl− Na+ Cl− Na+

FIG. 9. HOLE CENTRES IN SODIUM CHLORIDE (θ DENOTES HOLE)

U-Centres.

When sodium hydride is added to sodium chloride a new absorption band, termed the *U*-band, appears relatively far in the ultra-violet. Its precise position (*i.e.* of the wave-length peak) is 206 mμ.[122,123] For potassium chloride, containing potassium hydride, the *U*-band peak is at 217 mμ, while for potassium bromide the *U*-band is at 228 mμ.[31,122,124,125] Mott and Gurney[49] gave the model for the *U*-centre which is now generally accepted. It consists of a negatively charged hydrogen ion occupying substitutionally the position of a halogen ion; the hydrogen ion exhibits its characteristic absorption band.

U-centres can be converted into *F*-centres by irradiation with light in the *U*-band,[122,123] the quantum efficiency of this conversion increasing with increasing temperature from about 5% to 30–45% at temperatures between 20° and 220°C. *U*-centres may also be converted into *F*-centres by irradiating with *X*-rays at room temperature.[31] *F*-centres produced in this way are more stable than those produced by irradiation of the pure salt and are almost as stable as those produced by adding excess sodium.[32] It is more than likely that the *U*-centre → *F*-centre conversion occurs by the following mechanism.[31] A hole first of all annihilates one of the electrons on the hydride ion, the hydrogen atom so produced then diffuses away from that lattice site and the vacancy becomes occupied by an electron.

Z-Centres.

New absorption peaks[31,126] lying in the visible part of the spectrum, termed the *Z*-bands, appear when divalent ions such as those of strontium and barium are introduced into alkali halide lattices. Seitz[31] has discussed fully the structures of the *Z*-centres which give rise to such peaks, and it appears that there are at least three different kinds. The Z_1-centre, for instance, is believed to consist of the divalent ion and an attached electron in a positive-ion position. The Z_2-centre is believed to be the result of union of a Z_1-centre and a neutral pair of vacancies, while the Z_3-centre is a Z_2-centre which has captured a second electron.

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Dielectric Constant, Loss and Breakdown

Dielectric Constant.

Solid Sodium Chloride.

For all the alkali halides the dielectric constant for static fields, or for radio frequencies, is of the order of 5·0. Some of the values obtained for sodium chloride under these conditions are: 5·6,[1] 6·29,[2] 5·4,[3] 5·792,[4] 5·71[5] and 6·03,[6] but that now generally accepted is 5·62.[7-11]

The variation of the dielectric constant with temperature[10-13] between –190° and 550°C., and with pressure,[14] has been determined. After passing through a minimum, the position of which depends on the impurity content,[11] the dielectric constant begins to rise rapidly with increasing temperature between 500° and 520°C.[10]

The optical dielectric constant, ϵ, of the solid, derived from the relation $\epsilon = n^2$ where n is the refractive index, is 2·25.[7] The difference between the static and optical values may be attributed to ionic polarizability.[7] The Born equation[15] for this difference, $\Delta\epsilon$, gives a value of 2·7 which is in fair agreement with that observed. A later refinement of the Born equation by Szizeti[15] (see page 826) leads to an even closer agreement.

If solid sodium chloride contains water of crystallization its dielectric constant is increased,[16] and owing to the great influence of water vapour on the dielectric constant of the solid salt, it is possible to measure the rate at which water vapour is adsorbed on crystals of sodium chloride by following the change of the dielectric constant.[17] It has, in fact, been noted that a quantity of water as little as that required to form a unimolecular adsorbed layer gives rise to sharp peaks at about –30°C. in the temperature variation of the dielectric constant of sodium chloride.[18]

Aqueous Solutions.

In almost all the papers dealing with the dielectric constant of sodium chloride solutions published prior to 1940,[19-32] it is claimed that, for dilute solutions up to 0·025 N., the dielectric constant first of all falls linearly with increasing concentration and, after passing through a minimum, increases steadily to a value greater than that of water. After the theoretical significance of the effect of ions on the dielectric constant of water became fully appreciated, these measurements were carried out meticulously. They are now, however, of little use. This was realized once wave-guide techniques for the measurement of frequencies of the order of 10^{10} cycles sec.^{-1} were developed. It then became possible to measure with an accuracy of a few per cent. the dielectric constant of a conducting medium; and, consequently, the early data have been replaced by more reliable figures which are available for solutions of concentrations greater than 2 N.[33-36,37]

Sodium chloride and all the other uni-univalent electrolytes studied by Hasted, *et al.*,[34] cause the dielectric constant of water to fall linearly as the concentration of salt increases. This linear relation holds up to approximately 2 N., after which the drop is less than that demanded by the relation.[34] In the linear region, if ϵ_w is the static dielectric constant of water (78·54 at 25°C.),[35] ϵ^* that of the solution, and C the concentration of sodium chloride in moles l.^{-1} then

$$\epsilon^* = \epsilon_w + 2\delta C \dots\dots\dots\dots (1)$$

where δ, half the molar depression of the dielectric constant, is –5·5 at 25°C.[34] (The chlorides of potassium and rubidium each have $\delta = -5{\cdot}0$, whilst, for lithium chloride $\delta = -7{\cdot}0$).[34] Moriyama[37] has attempted to make a qualitative derivation of the dielectric constant–concentration formula for sodium chloride solutions at higher concentrations in terms of the interaction of Debye cavities.

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The formula he derived[37] is:

$$\epsilon^* = \epsilon_w(1 - \gamma c + \lambda\gamma^2 c^2) \ldots\ldots\ldots (2)$$

where γ is a constant characteristic of sodium chloride and water, and λ is a dimensionless constant. At 21·0° and 1·5°C., γ and λ are 0·15, 0·6 and 0·16, 0·39 respectively.[37]

An explanation has been given for the variation of the dielectric constant of aqueous sodium chloride solutions with concentration at low frequencies which throws light on the manner in which water molecules are oriented by sodium and chloride ions in solution.[38]

Measurements have been made of the dielectric constants of emulsions of 2 N-aqueous solutions of sodium chloride in petroleum.[39]

Dielectric Loss.

According to the modern theory of dielectrics,[40,41] the difference between the static or low frequency dielectric constant and the high frequency value, as measured by the square of the optical refractive index, may be largely ascribed to the damping out or relaxation of the orientational contribution to the dielectric constant. Much experimental work and many general discussions[40-43] of the chemical significance of loss angles and complex dielectric constants of ionic solids have been published.

From 10^3 to 10^6 cycles sec.$^{-1}$ the loss angle of dry rock salt is less than 0·0001, but the presence of moisture causes it to increase greatly, especially at low frequencies.[44] In the above frequency range the effect of exposure to X-rays[44,45] and cathode rays[44] has also been studied; and it was found that neither the former nor the latter rays had any measureable influence on the power factor. The effect of grain size on the magnitude of the apparent dielectric constant,[46,47] appears to be related to the influence of moisture, and a similar effect has also been noted at lower frequencies.[47] The large increase in the dielectric loss after grinding crystalline sodium chloride has been interpreted[47] in terms of the presence, before grinding, of highly conducting regions at the crystal surfaces due to adsorbed layers of water.[47]

Crystals of sodium chloride that have been annealed at temperatures as high as 550°C. display a dependence of dielectric loss on annealing temperature:[48] with increasing annealing temperature the dielectric loss at room temperature first increases for annealing temperature around 100° to 200°C. and then falls to a minimum for a temperature of 550°C. The yield point and ultimate strength of the crystal also show a similar dependence on annealing temperature suggesting a relationship between stress and dielectric loss.[48] This has been confirmed by the fact that deliberate stressing of the crystal causes an increased dielectric loss,[48,49] and also by the fact that plastically deformed sodium chloride crystals, when annealed thoroughly at high temperature, no longer display anomalous low-frequency dispersion.[50]

In single crystals of pure sodium chloride anomalous behaviour as to loss angle and dielectric constant has been noted at several frequencies near 3 megacycles sec.$^{-1}$.[51,52] At frequencies ranging from 500 to 4000 megacycles sec.$^{-1}$ the dielectric loss angle is inversely proportional to the frequency of the oscillation, a fact which can be plausibly explained by ionic vibrations.[53] At 1000 megacycles sec.$^{-1}$ a sodium chloride crystal has a loss tangent of 0·0002.[54]

The relation of the observed dielectric loss in alkali halide crystals to the presence of lattice defects merits comment here. It was Breckenridge[43,55] who first produced evidence for the existence of the vacancy pair type lattice defect. Following the classical Debye theory of permanent dipoles, he argued that the existence of a pair of cation and anion lattice vacancies, held together by electrostatic forces (see page 837), and their ability to orientate should constitute a relaxation process which should give rise to an anomaly in the dielectric loss at low frequencies. Such an effect was discovered by him,[55] and it has received considerable attention since.[43,55,56] Although there are some doubts[56] as to the validity of Breckenridge's conclusions, it is nevertheless certain that anomalous dielectric loss properties are exhibited by specimens of sodium chloride, especially in those to which impurities have been deliberately added. It may well be that these anomalies arise from a vacancy-impurity complex which has been identified, from electrical conductance measurements (see page 839), on sodium chloride containing cadmium chloride as an impurity. Haven,[56] who endeavoured without success to reproduce the results of Breckenridge and worked with single crystals of salt containing added traces of calcium and manganese, found one Debye peak for each impurity at about the same frequency. At 69°, 85°, 110° and 125°C. these frequencies, for calcium ion impurity, were, respectively, 1000, 2600, 12000 and 26000 cycles sec.$^{-1}$.[56] And the shift of the peak with temperature corresponded to an activation energy of about 0·7 e.V.[56]

Dielectric loss measurements have been carried out on aqueous solutions of sodium chloride in the frequency range 300–20000 kilocycles sec.$^{-1}$ over the concentration range 0·0005 to 0·5 N.[57] and on aqueous solutions varying in concentration from 0·0 to 3·0% by weight in the range of frequencies 230 to 330 megacycles sec.$^{-1}$.[58] Relaxation times obtained from such measurements agree fairly well with values calculated from the theories of Falkenhagen, Debye and Onsager. Accounts of these theories and of the chemical significance of dielectric measurements on sodium chloride solutions are available in published reviews.[41,42]

Dielectric Breakdown.

Facts relating to the breakdown of solid sodium chloride in strong electrical fields, both a.c. and d.c., have often been published for over thirty years. Unfortunately, much of the earlier work,[59-69] though it was valuable in determining which factors are important, has now been invalidated by the realization that only under stringent experimental conditions can reproduceable and significant results be obtained. Two important conclusions from the early work are (i) that dielectric breakdown, contrary to what had been initially suspected, does not involve ionic transport but is an electronic phenomenon,[62,69] and (ii) that when breakdown occurs, the electric discharge selects a definite path dependent on the orientation of the crystal.[62,63,64,66]

In the ensuing paragraphs, by dielectric breakdown (or dielectric strength) is meant breakdown of the intrinsic variety, quite distinct from thermal breakdown. Failure to recognize this was another factor which invalidated large sections of the pioneer work. Clear expositions of dielectric breakdown in solids have been given by Whitehead[70] and by O'Dwyer.[71]

For sodium chloride all the observed values of the dielectric breakdown are of the order of 10^6 V. cm.$^{-1}$, e.g. typical published values are (in million V. cm.$^{-1}$) 1·7,[72] 1·5,[73-75] 1·28[76] and 1·0.[77] The dielectric strength increases very slowly with increasing temperature from liquid nitrogen temperature up to about 50°C.[77-80] During impulse testing, with variation of the pulse time from 10^{-8} sec. up to a few seconds, the dielectric strength is independent of the pulse time.[71,77] It is also independent of the crystal thickness over the range 10^{-3} to 10^{-1} cm.,[71] and of the crystal orientation in the range from −195°C. to room temperature.[76,79,81] The actual path of the anodic discharge, *i.e.* the discharge initiated at the anode, is precisely oriented with respect to the crystallographic axes in the temperature range −160° to +325°C.[79] With increasing temperature in this range the discharge path follows the sequence: random → [100] → [111] → [110].[79]

Above temperatures around 50°C., where there appears to be some form of transition,[71] the dielectric strength falls slowly with increasing temperature, but its value is still independent of whether it is measured by d.c. or by pulses of about one microsec. duration.[71,79]

Calderwood *et al.*[82] found that the dielectric strengths of synthetic sodium chloride single crystals show considerable scatter which they attribute to differences in the extent of inherent faults in the crystals. Many of the latter were found to be appreciably stressed and by annealing beforehand the scatter was significantly reduced. The great importance of lattice deformation due to strain is now fully appreciated,[71,79,82,83] and it further invalidates the earlier observations because no precautions to safeguard against this e.g. by heat-treating the samples, appear to have been taken.

A lucid interpretation of these results in which the theories of von Hippel and Callen, Fröhlich, and Fröhlich and Paranjape are invoked is given in the article by O'Dwyer.[71]

In an isolated paper dealing with the electric breakdown of aqueous sodium chloride between two needle electrodes[84] it is stated that the breakdown is an electronic phenomenon, as for the solid, even though normal conduction through the solution is entirely electrolytic.

Some attention has been paid to the measurement of the dielectric breakdown of silver chloride and sodium chloride solid solutions at low and high temperatures,[85,86] and to the theoretical significance of the results.[87]

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Surface Tension and Surface Energy

The values of the surface tension of solid sodium chloride[1] determined directly by measuring the difference between the heat of solution of the ordinary crystalline salt and that of the finely divided salt at the same concentration are shown in Table XVI.

TABLE XVI.- SURFACE TENSION OF SOLID SODIUM CHLORIDE AT 25°C.

Diameter of average particle [a] (microns)	Surface tension (dynes per cm.)
1·00	395
1·16	406
1·14	356

[a] If the salt were composed of particles equal in size and of this diameter the area per mole would be the same as that actually observed.

Antonoff[2,3] found the surface tension to be 315 dynes per cm. for randomly oriented crystals, while a recent determination[4] gave a value of 366 dynes per cm. Kuznetsov and his coworkers,[5] by measuring the work required to split a rock-salt crystal, obtained a value of 150 dynes per cm. for the (100) face. According to Born and Stern,[6] the theoretical value of the surface tension of this face, derived by using their dynamic lattice theory, is 150·2 dynes per cm., but they point out that this, in fact, is in rough agreement with the surface tension of molten sodium chloride (106 dynes per cm. at 908°C., against nitrogen gas).[7] Born and Stern also state that the surface tension of the (110) face is 2·7 times that for the (100) face, whereas later work[8] has shown that the surface tensions of the (100), (110) and (111) planes are in the ratios $1:\sqrt{2}:\sqrt{3}$.

As the particle size of any solid is reduced, surface forces become progressively more important and should ultimately cause a gradual change in the unit-cell dimensions. This has been observed with sodium chloride,[9] the sign and magnitude of the changes being of the order predicted theoretically, provided surface layers of adsorbed gases are absent.

When molten sodium chloride is poured on to a rapidly spinning wheel, spherical particles of the salt are produced which are believed to possess an atomized surface or skin having a thickness of the order of 10^{-5} cm. From calorimetric, solubility and other measurements the surface energy of the atomized sodium chloride can be calculated, and it is found to be abnormal being of the order of 10^5 erg per cm.[28]

To account for the fact[10] that the surface area of finely divided sodium chloride decreases with increasing relative pressure, p/p^0, of water vapour in contact with the salt, it has been suggested[11] that ion pairs of sodium chloride are bound to the surface of the crystal with various binding energies. When water molecules are adsorbed on the surface at a particular relative pressure it is believed that ion pairs of a certain binding energy are loosened. These become mobile and can then migrate to lower energy sites, causing sintering, and hence a loss of surface area. This theory can be extended to explain the rapid initial reaction in the exchange of chlorine with a sodium chloride surface.[12]

Various investigators[13-20] have established that Quincke's rule, which linearly relates the surface tension of a solution to its concentration, is roughly obeyed by 1·0 to 5·0 M- aqueous sodium chloride solutions. The results obtained by Harkins and McLaughlin[14] are illustrated in Fig. 10.

The equation:[21]

$$\log(p/p_0) = -(K\Delta\sigma/RT),$$

where p_0 and p are the vapour pressures of solvent and solution, respectively, and $\Delta\sigma$ the difference in surface tension between them, satisfactorily describes

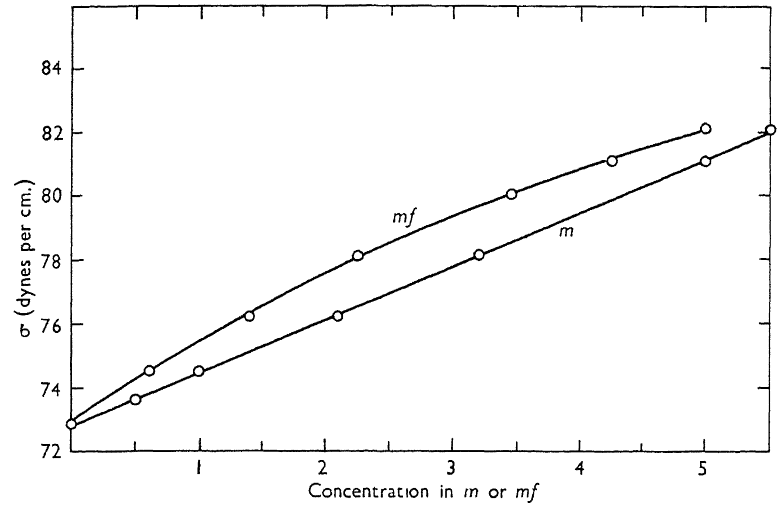

FIG. 10. THE VARIATION OF SURFACE TENSION (σ) OF AQUEOUS SODIUM CHLORIDE SOLUTIONS WITH MOLALITY (*m*) AND ACTIVITY (*mf*) AT 20°C.

the surface tension data for sodium chloride solutions.

The behaviour of very dilute sodium chloride solutions is quite complicated. The surface tension–concentration curve at 25°C.[19] has a steep negative slope up to about 0·001 M., where a minimum is reached, and from 0·001 to 0·005 M. it rises steadily and the surface tension is equal to that for pure water at 0·002 M. The initial decrease in surface tension at low concentrations, which shows that sodium chloride can behave as a 'capillary-active' substance, together with the well-defined minimum at about 0·001 M., has been observed[22,23] for aqueous solutions of potassium chloride, caesium iodide, and lithium fluoride and for solutions of eight other salts differing amongst themselves in valence type, size of ions and degree of hydration.

Neither the Onsager–Samaras[24] equation, based on the theory of interionic attraction, nor the Dole equation,[25] based on the hypothesis that the negative ion plays a dominant role in the adsorption of salts in the surface layer of water, adequately represents the whole of the concentration–surface tension curves. A more satisfactory equation combining the above equations has been derived.[23]

The temporary change of surface tension observed[26] when a fresh solution of sodium chloride is allowed to stand has been interpreted[26] in terms of ionic solvation and polymerization processes. An equation has also been derived[27] for the change with time of the surface tension of a solution, on the assumption that the delay in reaching equilibrium is due to the time required for the solute to reach the surface.

If σ_0 is the static surface tension of the solvent, σ that of the solution at a time t after the formation of the surface, and $\bar{\sigma}$ the static or ultimate surface tension of the solution, then:

$$\frac{(\sigma_0 - \bar{\sigma}) - (\sigma_0 - \sigma)}{(\sigma_0 - \bar{\sigma})} = \exp.[-2\sqrt{(t/\pi\tau)}]$$

The quantity τ, sometimes called the half-way time, is defined by:

$$\tau = \frac{(-d\bar{\sigma}/d\bar{c})_{\bar{c} \to 0}}{D\boldsymbol{R}^2T^2}$$

where $\bar{c}$ is the solute concentration per unit volume of solution, D is the coefficient of diffusion, and $\boldsymbol{R}$ and T have their usual meanings.

Tabulated results of the early determinations[29] of the surface tensions of sodium chloride in hydrochloric acid solutions at 20°C., and of mixed solutions of sodium chloride and sodium nitrate in mixtures of acetone and water at 20° and 40°C., are available. Results are also available[30] of early work on the surface tension–activity relationships of the system, urethane, sodium chloride and water. Later work[31] has explored the relationship between surface tension and the crystal habit adopted by sodium chloride when it crystallizes from aqueous solutions containing traces of other substances. Surface tension measurements were made on 30% sodium chloride solutions containing urea, hydrolyzed gelatin, human urine, cane-sugar molasses, butyl α-nitrosobutyrate and the sodium salt of a sulphonated naphthalene, all of which lowered the value for the 30% solution and tended to produce octahedral rather than cubic crystals on crystallization.

Detailed studies have been made of the surface tensions of ethyl alcohol–water–sodium chloride mixtures and acetic acid–water–sodium chloride mixtures.[32] Solutions of sodium chloride from 1·0–5·0 molal in aqueous alcohol (2·03 moles-%) give data which fit the equation:

$$(\partial\sigma)/(\partial_{m_1})_{m_2} = k_1\frac{\Gamma_1}{{}_0\Gamma_1} - \boldsymbol{R}T\Gamma_2(\partial \log f_2)/(\partial_{m_1})_{m_2}$$

where m is the bulk molal concentration, Γ is the surface concentration, f_2 the activity coefficient of ethyl alcohol, and the subscripts 1 and 2 refer to sodium chloride and ethyl alcohol respectively; ${}_0\Gamma_1$ is the surface concentration of salt in pure water at the same value of m, σ is the surface tension, k_1 a constant equal to 1·71, and $\boldsymbol{R}$ and T have their usual significance. By assuming that Γ_2 is independent of m_1 and using known values of f_2, the ratio $\Gamma_1/{}_0\Gamma_1$ can be calculated. The magnitude of this shows that in some cases the amount of water adsorbed is greater than that for an aqueous solution at the same concentration; in other cases it is less.

For acetic acid–water–sodium chloride mixtures $(\partial\sigma/\partial m_1)_{m_2}$ is positive and constant, being equal to 0·79 over the whole range of concentration of salt up to 4 molal. The aqueous acetic acid solutions contained 0·353 moles of acetic acid. The ratio $\Gamma_1/{}_0\Gamma_1$ is less than unity in this case and much less variable with concentration of salt than in the aqueous ethanol solution.

Determinations of the interfacial tensions[33] of aqueous sodium chloride solutions against various alcohols and esters reveal a minimum and a maximum in the tension at 0·05 × 10^{-3} and 0·5 × 10^{-3} M., respectively, which is interpreted in terms of hydrogen bonding. Curves showing interfacial tensions of mixed aqueous solutions of sodium chloride and cupric chloride against butyl acetate and of mixed solutions of sodium chloride and cobaltous chloride against *iso*amyl acetate[34,35] indicate the formation of the following complexes: $3NaCl,CuCl_2$, $2NaCl,CuCl_2$, $NaCl,CuCl_2$ and $NaCl,2CuCl_2$, at various concentrations for the $NaCl$–$CuCl_2$–H_2O system, and similar complexes for the $NaCl$–$CoCl_2$–H_2O system. Lithium, potassium and ammonium chlorides also form complexes of the above type with cupric and cobaltous chloride solutions.

Heymann *et al.*,[36] measured the surface tension of a molten mixture of sodium chloride and cadmium chloride and found that the values for an equimolar mixture were slightly less both at 700° and 800°C. (97 and 95 dynes $cm.^{-1}$ respectively) than those calculated for perfect or regular solutions using the Guggenheim equation,[37] which was derived on the assumption that the difference in composition of the surface from the bulk is confined to a unimolecular layer. The surface tensions at 700° to 1000°C. of molten salt mixtures containing sodium chloride, potassium chloride, calcium chloride and magnesium chloride have been determined by the maximum bubble pressure method.[38]

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General Mechanical Properties of Sodium Chloride

Under this heading the elasticity, plasticity, tensile strength, compressibility, hardness and other related properties of the salt are discussed. The modern interpretations of these properties for sodium chloride, as for other crystalline substances, are founded on the well established models of the defect solid state. Indeed, in this field more than any other in solid state physics, the impact of the theory of dislocations has been extensive. Detailed accounts of the theory of dislocations and its relevance to the solid state properties cited below have been given by Cottrell[1] and Frank.[2] The numerous investigations carried out prior to 1936 have been summarized and discussed

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by Schmid and Boas.[3]

Elastic Stiffness Constants.

The elastic stiffness constants (moduli of elasticity) c_{11}, c_{12} and c_{44}, defined[3] by relating linearly the stress components to the strain components, are known with good accuracy at several temperatures for single crystals of sodium chloride.[4-9]

The ultrasonic pulse method[8,9] yields the most reliable results, and at 300°K. these are:[9,10] c_{11} = 4·87, c_{44} = 1·26 and c_{12} = 1·24 × 10^{11} dyne cm.$^{-2}$. The variations with temperature of c_{12} and c_{44} are very slight, but c_{11} decreases steadily with rising temperature up to the melting point where its value is approximately 2·4 × 10^{11} dyne cm.$^{-2}$.[4-6,9] At absolute zero the extrapolated values of the constants are:[9] c_{11} = 5·750, c_{44} = 1·327 and c_{12} = 0·986 × 10^{11} dyne cm.$^{-2}$. Theoretical calculations[11-14] have given values of 1·515 and 1·032 × 10^{11} dyne cm.$^{-2}$ at absolute zero for c_{44} and c_{12} respectively.

It can be seen that the Cauchy relation[3] which, for cubic symmetry, is $c_{12} = c_{44}$, is moderately well satisfied in sodium chloride, a result which is not surprising in view of the predominance of electrostatic interaction of the ions in the crystal.[15]

From elastic stiffness constants it is possible to calculate the Debye Characteristic Temperature, Θ, of sodium chloride.[5,9,10] Typical values of the latter found in this way are 322° at 0°K.,[10] 292·6° at 0°K.[9] and 320° at 80°K.[5] These values are in good agreement with those derived from thermal data, e.g., at 0°K. the latter is 308°K.[15]

Elastic Compliance Constants.

For sodium chloride, as for all other cubic crystals, the compliance constants s_{11}, s_{12} and s_{44} are related to the stiffness constants by:[15]

$$s_{11} = (c_{11} + c_{12})/(c_{11} - c_{12})(c_{11} + 2c_{12})$$
$$s_{12} = -c_{12}/(c_{11} - c_{12})(c_{11} + 2c_{12})$$
$$s_{44} = {}^{1}/c_{44}$$

The validity of these relations has been confirmed experimentally,[16-21] and typical values obtained by the piezoelectric oscillator method are shown in Table XVII.[22] The experimental determinations of the elastic compliance constants of the alkali metal halides, and the significance of the results, have been comprehensively treated by Huntington.[23]

TABLE XVII.- ELASTIC COMPLIANCE CONSTANTS OF SODIUM CHLORIDE

Temp.°C.	s_{11}	s_{44}
	(× 10^{13} cm.^{2} dyne^{-1})	
27	22·90	78·41
77	24·01	79·38
127	25·30	80·45
177	26·71	81·57
227	28·23	82·75
277	30·00	84·01

Although compliance and elastic constants of solids are usually dependent only on the strain, it has occasionally been observed that they are affected by slight differences in the structure or history of the specimens.[1,23,24] Such effects have been observed for sodium chloride, and the significance of this unelasticity has been discussed by Breckenridge[25] and Huntington.[23]

Young's Modulus.

By measuring the deflection of a bar of sodium chloride under a load applied to its mid point, the Young's modulus was calculated as 4·0 × 10^{11} dyne cm.$^{-2}$.[26,27] This value agrees quite well with that calculated from the elastic constants quoted above, 4·1 × 10^{11} dyne cm.$^{-2}$.[26] The Young's modulus of sodium chloride has also been determined near the melting point of the solid.[28]

The Elastic Limit.

One recent determination reported the elastic limit of pure sodium chloride as 2·4 × 10^{7} dyne cm.$^{-2}$.[26] All the published values for rock salt specimens of different origin fall between about 0·1 and 3·2 kg. mm.$^{-2}$.[29-31] Experiments on the phase retardation of light as a function of load on a crystal of natural rock salt gave an elastic limit in the region of 19·0 g. mm.$^{-2}$.[32,33] The elastic limit is, however, very sensitive to pretreatments such as exposure to *X*-rays, to thermal annealing or to the addition of impurities. Kutnetzov and Sementzov[34] found that although the modulus of elasticity of rock salt is unchanged, its elastic limit is raised by 35% after irradiation with *X*-rays until coloured. A similar experiment showed an increase of 75·6%, the effect of ultra-violet light and *X*-rays being identical.[35,36] Regardless of the previous mechanical or thermal treatment, annealing at 600°C. for a few days decreases the elastic limit of rock salt crystals,[37] whereas addition of traces of impurity such as plumbous chloride[37] or strontium chloride[38,39] causes a reverse effect. The limit of elasticity can be increased several times to the limit of stability by residual deformation, but this strengthening is accompanied by weakening in the opposite direction.[40] A crystal that has been strengthened or weakened in this way relaxes after some time and approaches normal condition.[40] A lowering of the value of the elastic limit results from repeated straining almost to the elastic limit and retempering, showing the existence of a fatigue effect.[41] A precise study[42] of fatigue in single crystals of rock salt has revealed that the presence of a scratch parallel to the edge of the cube and perpendicular to the direction of the applied force greatly accelerates the process of failure by fatigue.

The slow deformation (creep) of rock salt under small stress - less than that corresponding to the elastic limit - has been studied.[43-45]

Tensile Strength.

There have been very many determinations of the tensile strength or tenacity of rock salt single crystals.[3] Ewald[46] concluded that the ultimate tenacity of a square prism of rock salt was 0·57 kg. mm.$^{-2}$, whereas Blank[47] stated that the tensile strength of the 'purest natural rock salt crystals' was less than 0·217 kg. mm.$^{-2}$ and probably less than 0·15 kg. mm.$^{-2}$. Another study[48] arrived at values of 0·2 to 0·5 kg. mm.$^{-2}$. The variation is due not so much to the application of non-uniform stresses during measurement, as had at one time been supposed,[48] but rather to variations in the history of the specimens, as for the variation of the elastic limit.[49] Annealing rock salt specimens of different origin at 600°C. for several hours substantially equalizes their tenacity which initially differed very considerably.[3,50,51] After annealing, the value of the common tensile strength is approximately 0·17 kg. mm.$^{-2}$,[3,47] the fracture planes being (100).[3] Addition of traces of impurity influences the tenacity of rock salt,[3,52-55] and if two added constituents, which separately form solid solutions with rock salt, are simultaneously present in small quantities, the strengthening effect is additive.

The temperature dependence of the tensile strength of rock salt varies according to whether or not the load is increased rapidly in the course of the actual test.[3,56,57] When loading is rapid, tensile strength can be determined at various temperatures without being affected by tensile strengthening, and under these conditions natural rock salt crystals give a virtually constant value of approximately 0·45 kg. mm.$^{-2}$ within the temperature range −190° to +600°C.[3] With slower loading however, the results are different.[3] The tensile strength remains sensibly constant from −270° to approximately −200°C., being in the region of 0·5 kg. mm.$^{-2}$. It then decreases slowly as the temperature rises, reaches a minimum at about +40°C., and increases rapidly at higher temperatures to about 4 kg. mm.$^{-2}$ at 400°C. These results have been discussed by Schmidt and Boas.[3]

With regard to the influence of crystal orientation upon tensile strength, the theoretical strength to be expected for rock salt should be in the ratios 1:2:3 for the (100), (110) and (111) directions respectively.[3] The observed ratios are 1:2·24:3·32, when based on maximum values, and 1:2·22:3·51 when based on mean values. These results have also been discussed by Schmidt and Boas.[3]

On comparing the observed value of the tensile strength with that calculated theoretically, the interesting fact emerges that the latter is many times the greater,[58-61] Ketelaar[61] has pointed out that the experimental value of 0·5 kg. mm.$^{-2}$ increases to 160·0 kg. mm.$^{-2}$ if the salt is immersed in water, a value approaching the theoretical tensile strength, 200 kg. mm.$^{-2}$. The reduction in the disparity between the theoretical and experimental tensile strength brought about by immersion in water was first observed by Joffé in 1924 and it is now known as the Joffé effect. Since then, many attempts[62-79] have been made to establish the relevant facts and a few explanations of the phenomenon have been formulated.[62,80-82]

Dealing first with the facts of the Joffé effect for rock salt, it is quite certain that water causes an appreciable increase in the plasticity of the crystal as well as in the tensile strength.[62] Enhanced tensile strength is always observed if the crystals are subjected to a given load and then surrounded with water up to a certain level.[62] But it is not essential that the dissolution of the crystal should take place while the specimen is loaded, e.g. unloaded crystals which have been immersed in water and tested immediately after drying exhibit values of tensile strength which are almost as high, providing dissolution has gone far enough.[64] In general, the greater is the extent of dissolution the greater is the tensile strength. Immersion in other liquids will also lead to enhanced tenacity: the Joffé effect has been observed for sodium chloride in concentrated sulphuric acid,[65,68] concentrated aqueous ammonia,[68] aqueous alcohol,[83] saturated aqueous sodium chloride,[84-86] paraffin oil,[86] benzene,[86] methanol,[86] ethanol,[86] ether,[86] xylene,[86] acetone[86] and carbon disulphide.[86]

According to the interpretation proposed by Joffé himself,[62] the increased tensile strength resulting from dissolution of the crystal arises because of the elimination of surface cracks and any other surface defects. Joffé's theory, in effect, states that the inherent tensile strength of the crystal is not raised by the dissolution, and that the apparent or technical strength obtained in the normal tensile test is less than that of the true tenacity owing to the presence of fine cracks on the crystal surface. The main difficulty with this theory is that it assumes a very great depth for the surface cracks, since no significant increase in strength is produced until a relatively large part of the crystal has been dissolved.[3,80] An alternative theory[80] attributes the enhanced tensile strength to preceding deformation: it is assumed that the tensile strength of an undeformed crystal is small, and that it reaches the high value calculated theoretically only as a result of deformation. According to this concept the effect of the water, or any other liquid is merely to remove the impediments from the crystal surface and therefore to assist deformation. In view of certain difficulties implicit in the latter explanation, Smekal[82] combined both the above theories and suggested that the Joffé effect is the result of work hardening. But, so far, no completely satisfactory theory which can accomodate all the experimental facts, has yet been formulated.[86]

Glide and Plastic Deformation.

Systematic studies of glide or slip and allied phenomena in ionic crystals, represented chiefly by work on sodium chloride, have been continuing for over thirty years.[87–102] An excellent account of the earlier work on initiation of glide, dodecahedral glide and mechanical twinning, with special reference to sodium chloride, has been given by Schmidt and Boas.[3] More recent, though less exhaustive, reviews are also available.[1,2,96,98,101] These correlate glide and other physical and mechanical properties of the salt.

Plastic bending of rock salt takes place by a glide process along $\{110\}$.[1-3,103-105] This permanent bending or plastic deformation has been extensively studied using both rock salt and sodium chloride crystals,[103-120] and the acquired knowledge of the geometry of the deformation, together with the critical value of the shear stress required for the initiation of glide on a substantial scale, has helped to elucidate the mechanism of the process.[1,2] The plastic bending of sodium chloride crystals indicates that dislocations are present in the crystal and that these exhibit a more or less static distribution.[1]

It is gratifying to note that the presence of lattice dislocations in sodium chloride may be demonstrated experimentally (i), by adding excess metallic sodium, which renders them visible[121] (network nodes are preferentially decorated and screw dislocations[1] do not appear to be revealed at all in this way); (ii), by phase-contrast microscopy and electron microscopy[122,123] which, when used before and after evaporating the crystal, reveal screw dislocations such as spirally wound steps and spiral pits[122,124] and, (iii), by depositing very thin films of metals such as silver, gold and zinc on to a single crystal and noticing their aggregation along surface blemishes,[125] such surface blemishes being formed by stresses less than a tenth of the strength of the salt.

In X-ray Laue photographs of bent or permanently deformed crystals, long distorted spots appear in contrast to the sharply defined dots produced by the normal crystal.[3] This phenomenon is known as asterism, and it has been observed with crystals of sodium chloride.[1,126–137] It is found, however, that the asterism in the X-ray Laue photographs of worked sodium chloride crystals does not take the usual form of continuous streaks but appears instead as strings of spots.[1,138] The break-up of the asterisms into spots has been interpreted as the result of alignment into walls of the edge dislocations introduced by bending.[1] Since the walls are arranged in a polygonal formation, the alignment process is called polygonization.[1,138,139]

Polygonization is a special form of a more general process known as recrystallization which may be regarded as the abrupt formation of unhardened crystal nuclei during the recovery of a plastically deformed specimen to its original condition. Recrystallization of sodium chloride has been carefully studied by Tammann,[140] Müller,[141] Przibram[142,143] and others;[144–146] Przibram[142] was able to demonstrate the phenomenon spectacularly in a slow-motion film. Muller[141] found that the speed of recrystallization increases with the degree of deformation and the annealing temperature; and all these workers found many similarities between the effect in sodium chloride and other alkali metal halide crystals and the effect in metals. Cahn,[139] who worked with crystals of magnesium, zinc, aluminium and rock salt has recently confirmed this. An admirable account of the theory of recrystallization with special reference to metal crystals has been given by Cottrell.[1]

When a single crystal of sodium chloride is plastically deformed in an inhomogeneous manner, a transient electric current flows through the crystal, even when no external electric field is applied. This effect was observed[147] when the deforming load was applied to a smaller area on one face of the specimen than on the other. The greatest charge flow occurs when a given stress is applied to the crystal for the first time: re-application of the same stress gives much smaller effects. As regards the direction of the current, negative charge flows in the external circuit away from the side of the crystal to which the higher stress is applied. The application of an external electric field, even as great as 1000 V. cm.$^{-1}$, exerts little influence on the effect.[147]

Hardness.

The Brinell hardness of sodium chloride, based on the diameter of the indentation formed on the cube plane with a load of 5 kg. and a ball diameter of 0·71 cm., is 12·4.[3,148] The hardness decreases with increasing temperature,[148,149] but increases with compression.[148] It is also sensitive to the quantity of the crystal surface. Thus, the adsorption of a polar molecule can cause a substantial reduction in hardness by reducing the cohesive forces near the crystal surface.[3,150] In recent years, however, results have been obtained which showed that the Brinell hardness of sodium chloride was not affected by moistening the solid with water, ethanol, castor oil or oleic acid,[157] and it has even been proposed[152] that sodium chloride should be used as a standard for microhardness tests in view of this indifference to changes in the laboratory atmosphere.

The Knoop hardness number of sodium chloride with 200 g. indenter load is reported as 15·2 with a (110) direction for the indentation and 18·2 with a (100) direction.[26]

Partington[175] has fully discussed the hardness of ionic crystals, methods of determining it, and its relation to other properties.

Cleavage.

Cleavage often affords the simplest method of preparing flat surfaces on single crystals.[153] Sodium chloride and other cubic materials cleave on (001), and the process may be effected, at room temperature, with a razor blade.[153-157] To cleave rock salt crystals on the (110) surfaces requires 1·76 times as much energy as cleavage in the (001) surfaces.[158]

A review of the work on the cleavage of sodium chloride up to 1933, including a theory of cleavage, has been published.[159]

Compressibility.

Slater[160,161] made accurate measurements at 30° and 75°C. of the compressibility of alkali metal halides up to 12000 atm. using the techniques devised by Bridgman[162] and others.[163,164] At 30°C., the compressibility of sodium chloride is $4{\cdot}20 \times 10^{-12}$ cm.^{2} dyne^{-1}.[160] By extrapolation, Slater calculated the compressibility at absolute zero as $3{\cdot}3 \times 10^{-12}$ cm.^{2} dyne^{-1}. He also found the change of compressibility with pressure to be independent of temperature between 30° and 75°C.[160,161] In more recent years, the coefficient of compressibility of the solid salt has been determined at temperatures between 5° and 80°C. up to pressures of 45000 kg. cm.$^{-2}$.[165-168] Przibram[3,169] discovered a simple relationship between the actual compression of crystalline rock salt and the applied pressure. If s is the compressive strain, defined by $s = (l_0 - l)/l$, where l_0 is the initial length and l the final length under a pressure p, and λ is defined by $\lambda = l_0/d$, where d is the length of the edge of the crystal cross-section, then: $s = b\lambda p$ the constant b being 0·0020 cm.^{2} kg.$^{-1}$. This relationship holds good at pressures upwards of 2000 kg. cm.$^{-2}$, and similar relationships are valid for all the chlorides, bromides and iodides of sodium and potassium.[3,169]

Szigeti[170] has made some interesting calculations on the relation between the compressibilities and characteristic absorption frequencies of alkali metal halides. He derived the equation:

$$\frac{1}{K} \approx \frac{\epsilon_0 + 2}{6(n^2 + 2)} \, (m\omega_t^2/a)$$

in which K is the coefficient of compressibility, ϵ_0, the dielectric constant for static frequencies, ω_t is the eigenfrequency of the transverse optical branch, *m* is the atomic weight of the cation, *a* is the nearest neighbour distance in the crystal lattice and *n* is the refractive index.

The coefficient of compressibility thus calculated is 0·99 of the experimental value.[170]

Compressibility of Sodium Chloride Solutions.

For aqueous solutions of sodium chloride, the coefficients of compressibility have been determined at 25°C. between pressures of 100 and 300 megabars,[171] at 35°C. between 100 and 300 metric atm.,[172] and at several temperatures in the supercritical region.[173] In the interpretation of the data, it is assumed that molecules of water which are attached to the sodium and chloride ions are already compressed to their maximum extent by intense electric forces round the ions, and that, on increasing the pressure, only the remaining free water molecules are compressed. It is thus possible to derive the number of water molecules in the former state (*i.e.* the hydration number) from compressibility data.[174] The hydration number determined in this way is 7 - twice the value derived from activity data for sodium chloride solutions.

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Specific Heat of Sodium Chloride

The specific heat of solid sodium chloride has been accurately measured over the temperature range 13° to 1500° K.[1-6] One formula[1] that describes the temperature variation satisfactorily between 20° and 800°C. is:

$$c_p = 0{\cdot}2006 + 0{\cdot}00007024\ (t - 20) - 37{\cdot}5 \times 10^{-9}\ (t - 20)^2$$

The value now accepted[6] for the molar heat capacity of the solid at 298·16°K. is 11·88 g.-cal. deg.$^{-1}$ mole^{-1}.

The measured values of the specific heat at low temperatures[4,5] have been compared[5] with those derived theoretically from the Debye theory, and a full discussion of the general theory of specific heat of crystalline solids with reference to sodium chloride has been given by Partington.[25]

The specific heats of mixtures of sodium chloride with one of the following salts have been determined:[7,8] sodium nitrate, potassium nitrate, sodium nitrite, potassium chloride, calcium chloride and barium chloride. It is found[7] that the total specific heat is not additive if the salts dissociate in the molten state, and that it reaches a maximum after a certain overheating of the mixed salts above their melting points.

The calorimetric determination of the specific heat of aqueous solutions of sodium chloride at concentrations from infinite dilution up to 3·0 M. and at temperatures from 20° to 35°C. has been described.[9-15] Table XVIII gives a selection of data in this range.[14] If p is the weight percentage of anhydrous salt, c_t is the specific heat at a temperature t(°C.), and c_{20} is the specific heat at 20°C. [$c_{20} = 0{\cdot}6516 + (0{\cdot}3475)(0{\cdot}96285)_p$], g.-cal.$_{15}$ g.$^{-1}$ per °C., then[14]

TABLE XVIII.- THE SPECIFIC HEAT OF AQUEOUS SODIUM CHLORIDE SOLUTIONS[14]

wt. %. anhyd. salts	Specific Heat in Joule g.$^{-1}$ deg. C.$^{-1}$ ± 0·1% −10°C.	0°C.	10°C.	20°C.	30°C.	10^4a (see eqn. 1)	10^6b
5		3·911	3·921	3·931	3·940	2·3	0
6		3·862	3·874	3·886	3·896	2·6	−1
7		3·816	3·830	3·843	3·854	2·8	−2
8		3·771	3·787	3·801	3·813	3·0	−3
9		3·730	3·747	3·761	3·772	3·0	−4
10		3·689	3·708	3·723	3·734	3·1	−5
11		3·651	3·670	3·686	3·697	3·2	−5
12		3·615	3·635	3·650	3·661	3·2	−5
13		3·580	3·600	3·615	3·627	3·2	−5
14		3·547	3·567	3·583	3·593	3·1	−6
15	3·491	3·516	3·536	3·551	3·561	3·0	−6
16	3·463	3·487	3·506	3·520	3·530	2·8	−6
17	3·435	3·458	3·477	3·491	3·500	2·7	−6
18	3·409	3·432	3·450	3·463	3·471	2·5	−6
19	3·384	3·406	3·423	3·435	3·443	2·3	−6
20	3·361	3·382	3·398	3·409	3·415	2·0	−6
21	3·338	3·358	3·374	3·384	3·389	1·8	−6
22	3·318	3·337	3·351	3·359	3·363	1·5	−6
23	3·298	3·315	3·328	3·336	3·340	1·5	−5
24	3·279	3·295	3·306	3·313	3·316	1·2	−5
25	3·261	3·276	3·286	3·292	3·293	0·9	−5

Conversion Factor: 1 Joule g.$^{-1}$ per°C. = 0·2389 g.-cal.$_{15}$ g.$^{-1}$ per°C.

$$c_t = [c_{20} + a(t - 20) + b(t - 20)^2]\ \text{g.-cal.}_{15}\ \text{g.}^{-1}\ \text{per}\ ^\circ\text{C} \ldots\ldots\ldots\ldots (1)$$

and the values of *a* and *b* are shown in Table XVIII.

Determinations have also been made at higher temperatures (below 80°C.) using both the isothermal[16-18] and adiabatic[19] methods. The data given in Table XIX are accurate within ±0·5%[18] and were obtained using the isothermal calorimeter.

TABLE XIX.- SPECIFIC HEAT OF AQUEOUS SODIUM CHLORIDE AT HIGHER TEMPERATURES

Moles of NaCl per 1000 g. of water	Specific Heat (g.-cal./°C.) 50°	75°
0·20	0·9840	0·9880
0·50	0·9645	0·9686
1·25	0·9236	0·9355
2·50	0·871	0·8695
5·55	0·787	0·780

Recent data[20] on the specific heat of aqueous sodium chloride solutions up to still higher temperatures (below 140°C.) have been interpreted[20] semi-empirically.

The specific heats of brines are available in tabulated form.[21]

Thermal Conductivity

Eucken and Kuhn[22] measured the thermal conductivity of solid sodium chloride and rock salt samples, taken from different sources, between −190° and 0°C. The presence of impurities and the source, whether synthetic or not, caused significant variations in the conductivity, and this decreased with increasing temperature. Others[23,24] have shown that a relationship of the form:

$$\lambda = \frac{c_1}{T} - c_2 \text{..........(2)}$$

where λ is the thermal conductivity, c_1 and c_2 are constants and T is the temperature in °K., holds for rock salt crystals up to 700° K.

For sodium chloride at 0°C. the thermal conductivity is 0·0238 g.-cal. cm.^{-1} sec.^{-1} deg.^{-1}, and at 83°K., it is 0·0902 g.-cal. cm.^{-1} $\text{sec.}^{-1}$$\text{deg.}^{-1}$.[22] (The thermal conductivity of halite is 0·0167 g.-cal. $\text{cm.}^{-1}\text{sec.}^{-1}\text{deg.}^{-1}$).

Despite the classical work of Peierls,[26] following the pioneer work of Debye, on the theory of the thermal conductivity of insulating solids, there are still no quantitative expressions available for the thermal conductivity of simple ionic substances such as sodium chloride in terms of the equilibrium properties of the solid. It is, however, generally agreed[26,27] that the magnitude of the conductivity depends essentially on the anharmonicity of the interatomic potential, so that one can expect a close relationship between the thermal conductivity and the coefficient of thermal expansion which also depends on the anharmonicity. Dugdale and MacDonald,[27] following Peierls,[26] have made the plausible assumption that

$$l \simeq (c/\alpha\gamma T) \text{..........(3)}$$

where l is the mean free path of the lattice vibrations (*i.e.* the mean free path of the 'phonons'), c is the shortest distance between unlike ions ($c = (a/2)$, where a is the lattice constant), α is the coefficient of thermal expansion, γ is the Gruneisen parameter (see page 782) and T is the absolute temperature. The thermal conductivity is related to the mean free path of the lattice vibrations by:

$$\lambda \simeq \tfrac{1}{3} C_v \, l \, u \text{..........(4)}$$

where C_v is the specific heat per unit volume of solid and u is the velocity of sound in the solid. Using published data Dugdale and MacDonald[27] calculated that at 0°C. the thermal conductivity of sodium chloride is 0·028 g.-cal. $\text{cm.}^{-1}\text{sec.}^{-1}\text{deg.}^{-1}$ which, on comparison with the experimental value 0·024 g.-cal. cm.^{-1} sec.^{-1} deg.^{-1}, demonstrates that equation (4) is reasonably satisfactory. Agreements of this degree between the calculated and experimental values of λ for eight other alkali metal halides have been obtained.[27]

The thermal conductivity of aqueous salt solutions can generally be described by the equation:[25]

$$\lambda_S = \lambda_W \, (1 - 10^{-5} x \, p) \text{..........(5)}$$

where λ_W is the thermal conductivity of water at the same temperature as applies to λ_S, the conductivity of the solution. In equation (5), p is the number of grams of solute per 100 g. of solution and the value of x is characteristic of the dissolved salt. When λ_S and λ_W are expressed in watts cm.^{-1} deg.^{-1} (1 watt cm.^{-1} deg.^{-1} $\equiv$ 0·239 g.-cal. cm.^{-1} sec.^{-1} deg.^{-1}), then x = 248·0 and the values of λ_W at 17·8°, 20° and 32°C. are 583 × 10^{-5}, 587 × 10^{-5} and 606·8 × 10^{-5} watt cm.^{-1} deg.^{-1} respectively.[25] Typical values of λ_S are, for p = 12·5 at 32°C., 587 × 10^{-5} watt cm.^{-1} deg.^{-1} and, for p = 25·0 also at 32°C., 570 × 10^{-5} watt cm.^{-1} deg.^{-1}.[25]

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Thermodynamic and Thermochemical Properties of Sodium Chloride

Table XX[1] gives the more important thermodynamic data for sodium chloride.

TABLE XX.- THERMODYNAMIC AND THERMOCHEMICAL PROPERTIES OF SODIUM CHLORIDE

Function	State	Value
ΔH_f^0 at 0°K. (kg.-cal. mole^{-1})	gas	−43·0
ΔH_f^0 at 0°K. (kg.-cal. mole^{-1})	solid	−97·755
ΔH_f^0 at 298·16°K. (kg.-cal. mole^{-1})	gas	−43·5
ΔH_f^0 at 298·16°K. (kg.-cal. mole^{-1})	solid	−98·232
ΔG_f^0 at 298·16°K. (kg.-cal. mole^{-1})	solid	−91·785
$\log_{10}K_f$ at 298·16°K. (kg.-cal. mole^{-1})	solid	67·2771
S^0 at 298·16°K. (g.-cal. deg. mole^{-1})	solid	17·30
C_p^0 at 298·16°K. (g.-cal. deg. mole^{-1})	solid	11·88
ΔH_f^0 at 298·16°K. (kg.-cal. mole^{-1})	aq. solution (unit molality)	−97·302
ΔG_f^0 at 298·16°K. (kg.-cal. mole^{-1})	aq. solution (unit molality)	−93·939
$\log_{10}K_f$ at 298·16°K.	aq. solution (unit molality)	68·8560
S^0 at 298·16°K. (g.-cal. deg.$^{-1}$)		27·6
Heat of Sublimation at 1081°K. (kg.-cal. mole^{-1})	solid → gas	51·5
Entropy of Sublimation at 1081°K. (g.-cal. deg.$^{-1}$)	solid → gas	47·6

continued on following page

TABLE XX.- continued

Function	State	Value
Heat of fusion at 1081°K. (kg.-cal. deg.$^{-1}$)	solid→liquid	6·8
Entropy of fusion at 1081°K. (g.-cal. deg.$^{-1}$)	solid→liquid	6·3
ΔC_p of fusion at 1081°K. (g.-cal. deg.$^{-1}$)	solid→liquid	0·8
Heat of vaporization at 1738°K. (kg.-cal. deg.$^{-1}$)	liquid→gas	40·8
Entropy of vaporization at 1738°K. (g.-cal. deg.$^{-1}$)	liquid→gas	23·5

Villa,[2] using published data to which reference is made here (e.g. ref. 3), has calculated the Gibbs free energies of formation of sodium chloride between 25° and 2000°C. His results are summarized below:

$$2\mathrm{Na}_{\mathrm{solid/liquid}} + \mathrm{Cl_2}_{\mathrm{gas}} \rightleftharpoons 2\mathrm{NaCl}_{\mathrm{solid}}$$
$$\Delta G_{298-1073°\mathrm{K.}} = -198050 + 47{\cdot}2\,T_{(\pm 1)}$$
$$2\mathrm{Na}_{\mathrm{liquid}} + \mathrm{Cl_2}_{\mathrm{gas}} \rightleftharpoons 2\mathrm{NaCl}_{\mathrm{liquid}}$$
$$\Delta G_{1073-1156°\mathrm{K.}} = -181200 + 31{\cdot}5\,T_{(\pm 1)}$$
$$2\mathrm{Na}_{\mathrm{gas}} + \mathrm{Cl_2}_{\mathrm{gas}} \rightleftharpoons 2\mathrm{NaCl}_{\mathrm{liquid}}$$
$$\Delta G_{1156-1738°\mathrm{K.}} = -225600 + 70{\cdot}0\,T_{(\pm 2)}$$
$$2\mathrm{Na}_{\mathrm{gas}} + \mathrm{Cl_2}_{\mathrm{gas}} \rightleftharpoons 2\mathrm{NaCl}_{\mathrm{gas}}$$
$$\Delta G_{1738-2300°\mathrm{K.}} = -120000 + 31{\cdot}8\,T\log T - 93{\cdot}8\,T\ (\pm 5)$$

The figures in brackets after each Gibbs free energy expression denote the limits of accuracy, in kg.-cals.[2]

The heat content of dilute[4-8] and more concentrated[9-10] aqueous solutions of sodium chloride, together with the integral[11-16] and differential[17-19] heats of dilution have been measured frequently at several temperatures. The data of Robinson and Gulbransen[14] for dilute solutions are shown in Table XXI.

TABLE XXI.- THE INTEGRAL HEATS OF DILUTION* OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

Molality m	ΔH_∞ in g.-cal. mole^{-1} of NaCl at temperatures (°C) of 25°	20°	15°	10°
0·0001	−4·2	−3·7	−3·4	−2·3
0·0005	−9·4	−8·2	−7·7	−4·3
0·001	−13·2	−11·6	−10·8	−7·5
0·005	−29·6	−26·0	−24·3	−16·9
0·01	−29·3	−36·2	−33·3	−23·9
0·05	−71·3	−63·5	−54·2	−40·6
0·1	−86·5	−70·0	−58·3	−38·6
0·2	−87·6	−68·3	−46·3	−18·3
0·404	−69·4	−42·3	−6·6	+27·2
0·816	−11·7	+23·5		

The integral heat of dilution, ΔH_∞, is the heat absorbed when a solution containing one mole of solute is diluted to $m = 0$.

It has been shown[20] that the data in Table XXI are in agreement with data on the temperature dependence of the activity coefficient of sodium chloride.

Heats of solution of sodium chloride in mixtures of ordinary water and deuterium oxide, D_2O, change linearly with increasing deuterium oxide content.[21,22] In pure water at 25°C. the heat of solution for a final concentration of 0·45 mole of salt per 100 mole of solvent is 1·019 kg.-cal; in pure deuterium oxide under identical conditions, the value is −1·577 kg.-cal.[21] Heats of solution of the salt in methanol-water mixtures (10 to 95 mole % of methanol) at 20°C.,[23] in formamide[24] and in liquid ammonia at −33·4°C.[25] have been determined. In liquid ammonia, for a final dilution of 174·5 moles of ammonia per mole of salt, the molar heat of solution is 1460 cals.[25]

Solvation.

From the measured integral heat of solution, the lattice energy of sodium chloride and other thermodynamic and thermochemical quantities it is possible to calculate, by means of a Born-Haber cycle, the heat and free energy of solvation. In this manner heats of solvation in water,[26,27] methanol[27] and ethanol,[27] together with the free energies of hydration in pure water[28,29] have been determined. At 25°C. the heat of hydration of sodium chloride is 178 kg.-cal. mole^{-1},[26] and the sum of the standard free energies of hydration of the sodium and chloride ions is 170·1 kg.-cal. mole^{-1}.[29] The actual hydration numbers of these ions have been evaluated from hydration heats.[26,30,31] Typical values of n, the number of water molecules surrounding the ion in the nearest solvate envelope, which have been obtained for the sodium ion and chloride ion are 6 and 8 respectively.[26] The hydration numbers determined using other methods[32-34] often agree well with these values, e.g., $n_{\text{Na}^+} = 7{\cdot}4$ as determined from ion transference number data (see page 872). Frequently, however, alternative methods of determining hydration numbers yield widely divergent results. For example, from salting out effects it may be calculated[34] that $n_{\text{Na}^+} + n_{\text{Cl}^-} = 22$, and a polarimetric method of studying the hydrolysis of ammonium molybdate in aqueous sodium chloride solutions indicates[35] a hydration number as high as 750. Such discrepancies, which are often due to failure to define precisely the difference between primary and secondary hydration, have been fully discussed.[36,37,38]

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Electrical Conductance of Sodium Chloride

This sub-section deals only with the conductance of sodium chloride at temperatures up to its melting point and under ordinary conditions. Photoconductance is considered elsewhere (page 799).

The detailed study of the electrolytic conductance of sodium chloride and other alkali halides over the last forty years has furnished the key for understanding the basic disorder of ionic crystals generally. The following facts have been established.

(i) Up to about 500°C. the conductance, σ, of sodium chloride varies with temperature according to the equation:

$$\sigma = A \exp. (-E/RT) \text{..........} (1)$$

where A and E are constants.[1-10]

(ii) At slightly higher temperatures (in the region of 550°C.) the $\log \sigma/(1/T)$ plot has a 'knee' which divides the graph into two distinct parts. For the complete range of temperature up to around 800°C. the conductance fits the equation:

$$\sigma = A_1 \exp. (-E_1/RT) + A_2 \exp. (-E_2/RT) \text{..........} (2)$$
$$(A_1 < A_2 \text{ and } E_1 < E_2)$$

where A_1, A_2, E_1 and E_2 are constants.[4,11-14]

(iii) In the low temperature region (below 500°C.) the constants of the above equations are inclined to vary from one sample to another and are sensitive to structure. Thus, artificially grown crystals have a conductance ten to one thousand times as great as natural crystals at 90°C.[15-19] Again, if a rock salt crystal is heated and cooled rapidly its conductance at a particular temperature is increased.[1,12,20-22] The application of stresses above the yield point also produces an increase in conductance.[20,23-25] Another factor causing variation in conductance from one sample to another is the influence of impurities, e.g. small quantities of foreign ions enhance the conductance,[7,16,19,20,26] especially where the cations have higher valency than sodium as in $CdCl_2$.

In the high temperature region (500° to 800°C.), on the other hand, the conductance is reproducible from sample to sample, and is independent of previous thermal history.[27]

(iv) In the low temperature region conductance occurs by transport of sodium ions only, the contribution of chloride ion movement and electronic conductance being negligible. In the high temperature region bipolar conductance obtains, but the electronic contribution is still negligible. Table XXII shows the results at different temperatures, the transference numbers, t_1 and t_2, having been determined by an adaptation of the classical technique used by Hittorf for solutions.[14,28-30] The absolute values found by the two groups of investigators are not in very good agreement, probably because of differences in the purity and pretreatment of the samples used. As a rule, the purer is the sodium chloride, the lower is the temperature at which the onset of bipolar conductance occurs.[27,28,31-33]

TABLE XXII.- THE TRANSFERENCE NUMBERS OF SODIUM (t_1) AND CHLORIDE (t_2) IONS IN SOLID SODIUM CHLORIDE

Temp. °C.	t_1	t_2	Investigators
400	1.00	0.00	Tubandt et al.[28]
425	1.00	0.00	
500	0.98	0.02	
600	0.95	0.05	
625	0.93	0.07	
604	0.59	0.41	Jost and Schweitzer[29,30]
657	0.35	0.65	
710	0.12	0.88	

(v) The continuous conductance of sodium chloride at high field strength (200kV.cm.$^{-1}$) depends markedly on the field strength up to temperatures of approximately 200°C.[2,3,34] The continuous conductance is defined by $\sigma_D = I_D/V$, where I_D is the continuous current and V the potential difference. (σ_D differs from the true conductance, σ_t, which is defined by $\sigma_t = I_D/(V-P)$, where P is the back potential). At field strengths of about 100kV.cm.$^{-1}$, Poole's equation[3,34] *viz.* $\sigma_D = a$ exp. (bE), where a and b are constants and E is the field strength, has been found to hold.

(vi) The conductance and self-diffusion coefficient (see page 850) at temperatures greater than 550°C. obey the Einstein relation:

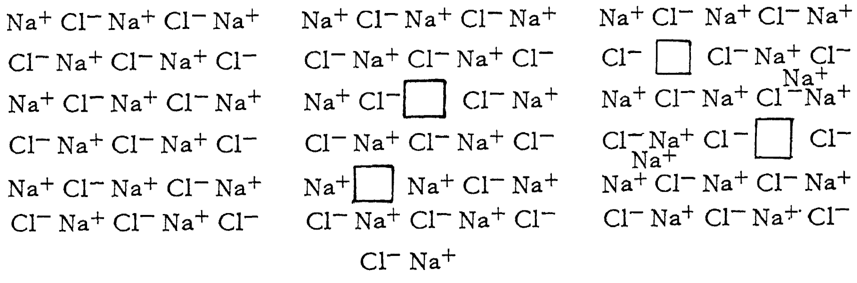
$$\frac{\sigma}{D} = \frac{Ne^2}{kT} \text{..........(3)}$$

where D is the self-diffusion coefficient, N is the total number of lattice sites, e the electronic change and k the Boltzmann constant.[26,27,35,36]

(vii) The activation energy of ionic conductance of sodium chloride at its melting point, calculated from its molar conductance, exceeds by eighty per cent the activation energy calculated from the specific conductance.[37]

Many of the above facts are largely explicable in terms of present knowledge of the structure of ionic crystals, full discussions of which are available.[27,38,39]

On experimental grounds and on the basis of both approximate and more rigorous calculations there is little doubt that the sodium chloride lattice contains Schottky defects, as shown in Fig. 11(b), rather than those first envisaged by Frenkel which are shown in Fig. 11(c).[27,40,41] Anion and cation vacancies are present in equal numbers but there are very few interstitial ions.



(a) Ideal Lattice (b) Lattice with Schottky Defects (c) Lattice with Frenkel Defects

FIG. 11. POINT DEFECTS IN SOLID SODIUM CHLORIDE

In the above figures both cation and anion vacancies have been given the same symbol, □.

It is generally accepted that the high temperature conductance of sodium chloride is due to the diffusion of vacancies through the lattice.[27] A vacancy migrates by virtue of an adjacent lattice ion jumping into the vacancy over a potential barrier. Hence, according to this mechanism, the conductance requires a certain energy, E, which is determined by the height of this potential energy barrier, U, and the energy, W, required to form a vacancy. It can be shown[27] that, for one type of vacancy, say cationic, the contribution made by cation vacancy migration to the total conductance is:

$$\sigma_1 = \sigma_1^0 \text{ exp. } (-E_1^0/RT) \text{..........}(4)$$

where $E_1^0 = U_1 + \frac{1}{2}W_1$, σ_1 is the cation vacancy conductance, and σ_1^0 is a constant calculable from other lattice parameters and fundamental constants. Experimentally, the values of U_1 and W_1 for sodium chloride are found to be 0·85 and 2·02 e.V. respectively,[27] while the theoretical values are 0·5 and and 1·86 e.V.[41] When both cation vacancy and anion vacancy migration contribute to the over-all conductance, the theoretical expression for σ includes two exponential terms:

$$\sigma = \sigma_1^0 \text{ exp.}\left(\frac{-E_1^0}{RT}\right) + \sigma_2^0 \text{ exp.}\left(\frac{-E_2^0}{RT}\right) \text{.........}(5)$$

The empirical equations (1) and (2) are therefore accounted for.

In the low temperature region the conductance of sodium chloride is much less amenable to quantitative treatment because of its irregularity. Several explanations have been proposed to account for the dependence of conductance in this range on structure, purity and thermal history, all of which are valid under certain conditions. The first, due to Smekal,[42] suggests that the conductance at low temperature will vary in a manner dependent on the number of grain boundaries and Smekal cracks that are present. Along the latter the migration of the ions will be free compared with the migration of vacancies through the lattice. This explanation is no doubt important in cases where the salt contains an extensive mosaic structure. The second suggestion is based on the concept of 'frozen equilibrium'.[40] The higher is the temperature of sodium chloride, the greater is the concentration of lattice defects; hence the greater is the concentration of anion and cation vacancies. If a crystal at a higher temperature is rapidly cooled, there is every likelihood that, owing to the smaller mobility of vacancies at lower temperatures, the concentration of vacancies corresponding to the higher temperature will be retained. Small changes in temperature in the low temperature region will then have no effect on the number of vacancies, and the variation of conductance with temperature in this region will be determined entirely by the mobility of the vacancies. The magnitude of the conductance at any particular low temperature will thus depend on the rapidity of quenching. When the purity of sodium chloride is high, this explanation of structure-sensitive conductance often applies. For example, a 'pure' rock salt specimen which has taken aeons to cool, and therefore contains relatively few defects, will exhibit a smaller conductance than an artificial specimen cooled under ordinary laboratory conditions. This can be seen from the simple equation for conductance:

$$\sigma = nev \text{..........}(6)$$

where n denotes the number of vacancies per unit volume, e the electronic charge, and v the mobility.

Another explanation for the low temperature conductance is based on the effect of crystal impurities. If a foreign cation of greater valency than sodium fills a cation site in an ideal sodium chloride lattice, the net effect, since electrical neutrality must be preserved, is the creation of a cation vacancy as shown in Fig. 12. Cation vacancies produced in this way will be present in the same concentration at all temperatures, but their effect on conductance

Na^+ Cl^- Na^+ Cl^- Na^+
Cl^- Na^+ Cl^- □ Cl^-
Na^+ Cl^- Na^+ Cl^- Na^+
Cl^- Cd^{++} Cl^- Na^+ Cl^-
Na^+ Cl^- Na^+ Cl^- Na^+

FIG. 12. EFFECT OF INTRODUCING A DIVALENT ION (Cd^{++}) INTO SODIUM CHLORIDE

will be greater the lower the temperature. Hence it follows that the low-temperature conductance is enhanced by adding certain impurities. The presence of other alkali halide impurities, such as potassium chloride, do not affect the vacancy concentration and so do not contribute to the anomalous low-temperature conductance. A simple quantitative theory based on this concept[43] can accomodate most of the results obtained by Etzel and Maurer,[31] who studied the effect of added cadmium chloride on the conductance of sodium chloride. A refinement[32] of the picture takes into consideration the extent of complex formation between the impurity ions and the vacancies (a cation vacancy, because it bears an effective negative charge, will tend to attract any positively charged species such as the impurity ion itself). There is definite evidence for the formation of a neutral 'complex' between cadmium ions and cation vacancies as the increase in conductance shown by sodium chloride with added cadmium chloride is not quite proportional to the mole fraction of cadmium.[31] An association energy of 0·35 e.V.[32] has been estimated for this 'complex', in close agreement with the theoretical value of 0·38 e.V.[44]

The early observations on the influence of large stresses on the conductance have since been interpreted in terms of recent developments in crystal dislocation theory.[45] The increased conductance accompanying the application of stresses results from the generation of vacancies from dislocations.

The fact that the Einstein relation (equation (3)) is obeyed means that both ionic conductance and self diffusion proceed by the same mechanism, migration via lattice defects.[35,36]

The significance of Poole's equation, which describes the variation of conductance with field strength has been discussed.[3,34]

Electrolysis of Pure Sodium Chloride.

When molten rock salt is electrolyzed the magnitude of the decomposition potential does not vary greatly with temperature, e.g. values of 3·20 V. at 800°C.,[46] 3·24 V. at 810°C.,[47] 3·15 V. at 820°C.,[48] 3·06 V. at 840°C.,[49] 3·11 V. at 900°C.[50] and 2·91 V. at 945°C.[49] have been obtained. At these temperatures, and below (300°–600°C.),[51,52] tree-like dendrites of sodium extend from the cathode in the direction of the anode. These structures will form at even lower temperatures if very high potential differences are used.[52] At 150°C., the lowest temperature at which dendritic structures have been observed, 20,000 V. per cm. of crystal thickness are required.[52]

Changes in temperature profoundly affect the cathodic current efficiency of the electrolysis. If it is assumed that the decreasing current efficiency (η) with rising temperature is due mainly to increasing solubility of the sodium in the fused salt, the following equation may be derived:

$$\log b = \frac{-a}{T} + \beta \ldots\ldots\ldots(7)$$

where b is the percentage of sodium lost through solution (whence $\eta = 100 - b$), and a and β are constants the values of which are 6120 and 7·94 respectively in the range 823° to 1033°K.[53]

The reaction occurring at the anode depends on the material of the electrode.

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For silver, coarse dendritic masses of silver chloride and sodium cyanide solid solutions are formed,[51] while pseudomorphic dendrites of lead chloride and a transparent layer of cupric chloride form on molten lead and copper anodes respectively.[51]

Between platinum electrodes at temperatures ranging from 400° to 600°C., the potential drop in a sodium chloride crystal is linear, but at both electrodes there are discontinuous potential jumps which amount to 16 to 60% of the 300 V. d.c. voltage applied.[54] From 600° to 700°C., application of 100 to 300 V. (d.c.) gives rise to a low-voltage counter e.m.f., the magnitude of which is approximately 1 V.[54]

Under the influence of an electric field, thin layers of ^{22}NaCl and ^{24}NaCl deposited on a single crystal of ordinary rock salt can be partially separated.[55] After 20 hr. at 700°C. under a potential difference of 10 V., an enrichment in ^{22}Na of from 10 to 20% was found at distances of about 1 mm. from the surface.[55]

The electrolysis of copper in rock salt over the temperature range 550° to 780°C. has been studied:[56] the logarithm of the mobility of the copper ions is proportional to the negative reciprocal of the absolute temperature.[56]

The Electrochemistry of Fused Mixtures Containing Sodium Chloride.

Extensive studies of binary, ternary and quaternary systems of fused salts have yielded information about the following electrochemical properties: electrode potentials of metals and metalloids, discharge potentials, decomposition potentials, current efficiencies, electrical conductances and transference numbers. At present, however, the theoretical appreciation of these properties is not commensurate with the reliability of the data. Consequently, the data have been used mainly for practical purposes, as in the electrowinning and isolation of metals.

Binary mixtures have received most attention. For a fused mixture of sodium and potassium chlorides, the specific conductance increases with increasing temperature, and is more temperature-dependent immediately above the melting point than at higher temperatures.[57,58] At any fixed temperature, the specific conductance shows marked, negative deviation from that predicted by the additivity law.[57] The current-voltage curves for this system at various temperatures yield a temperature coefficient for the decomposition potential of $-1{\cdot}501 \times 10^{-3}$ V. deg.$^{-1}$, which is close to the values for both the potassium iodide–rubidium iodide and potassium iodide–caesium iodide mixtures.[59] The electrical conductances of calcium and sodium chlorides have been measured in the temperature range 500 to 1100°C.,[60–62] and have been examined with a view to obtaining sodium by electrolysis of the fused mixture.[63] For this system also, the variation of conductance with temperature is considerably greater at lower than at higher temperatures, and again at a fixed temperature the conductance does not follow the additivity law.[60] The behaviour of sodium chloride–aluminium chloride mixtures under thermodynamically reversible and irreversible conditions has been explored from 160° to 700°C.[64–67] In addition to studies of the electrolytic conductance,[65] the polarization,[67] and the transference numbers of the sodium ion[66] in these mixtures, the electrode potentials at 300°, 500° and 700°C. for the following metals have been accurately determined:[64] lithium, potassium, barium, strontium, sodium, calcium, magnesium, beryllium, aluminium, thallium, manganese, zinc, cadmium, lead, tin, copper, mercury, silver, cobalt, nickel, bismuth and antimony. The decomposition potentials of sodium chloride–aluminium chloride mixtures with and without the chlorides of the above-mentioned metals,[64] of the sodium chloride–aluminium bromide system,[68] sodium chloride–silver chloride,[69] sodium chloride–plumbous chloride[69] and sodium chloride–zinc sulphate[70] systems have also been determined.

The conductance of sodium chloride–magnesium chloride[71] and sodium chloride–sodium pyrophosphate[72] mixtures at high temperatures, and the electrolysis of sodium chloride–ferric chloride[73] mixtures have been studied. The optimum conditions for the electrodeposition of iron during the electrolysis of the latter mixture are a temperature of 200°C., a current density of 0·77 amp. dm.$^{-2}$ and a cathode rotating at 700 r.p.m.[73]

A few publications have dealt with the electrochemistry of ternary mixtures based on a molten mixture of sodium and potassium chlorides to which has been added a third salt, usually a chloride. The electrolysis of a eutectic mixture of the chlorides of sodium, potassium and lead at 500°C., with lead as cathode and an anode containing 95% lead yields an electrodeposit of lead the impurity content of which is less than 0·01%.[74] The relative positions of anions in the sequence of increasing discharge potentials in fused equimolecular mixtures of potassium chloride and sodium chloride at 700°C. is: hydroxide, nitrate, sulphide, sulphate and chloride.[75] This sequence is not changed by additions of sodium sulphate up to 45% by weight to the alkali halide melt.[75] The electrolysis of sodium chloride–potassium chloride–nickel chloride,[76] sodium chloride–potassium chloride–strontium chloride[64] and sodium chloride–potassium chloride–magnesium chloride[77] has been studied from the viewpoint of current efficiency,[76] polarization potentials[76] and decomposition potentials.[64]

The decomposition potentials and the potentials of an inert electrode immersed in fused sodium chloride–aluminium chloride mixtures in the presence of other metal chlorides,[78] ethyl bromide,[79] and nitrobenzene[80] are known.

The fused mixture of sodium chloride–potassium chloride–magnesium chloride–calcium chloride is one of the few four component systems the electrical conductivity of which has been studied in detail,[81,82] probably because of its importance in electrolytic cells producing magnesium.

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Magnetic Properties of Sodium Chloride

The specific diamagnetic susceptibility of solid sodium chloride, and its variation with temperature, are shown in Table XXIII.[1]

TABLE XXIII.- DIAMAGNETIC SUSCEPTIBILITY OF SOLID SODIUM CHLORIDE

$10^6\chi$ (mass susceptibility; c.g.s. units)	Temp. °C.
−0·501	−150
−0·499	+ 18
−0·499	+362
−0·508	+933

For rock salt at 20°C. the specific susceptibility is −0·50 × 10^6 c.g.s. units.[1] All these values were determined prior to 1929, but they agree quite well with values obtained subsequently,[2-4] e.g. the molar diamagnetic susceptibility of the solid, determined by the Goüy method, was found to be −30·2 × 10^{-6} c.g.s. units by Hoare[4] and −30·1 × 10^{-6} c.g.s units by Hocart.[2]

The distribution of electrons in solid sodium chloride, as determined by *X*-ray reflection experiments, has been used to calculate theoretically the diamagnetic susceptibility of the salt, and the results obtained served to check the validity of the calculated electron distribution.[5]

As mentioned earlier in connection with the occurrence of colour centres, sodium chloride may, in certain circumstances, be rendered paramagnetic. If the crystal contains *F*-centres, whether these have been produced by *X*-rays or by adding a stoicheiometric excess of metallic sodium, there is at each centre an impaired electron in an *s*-state. Hence, if the concentration of *F*-centres is high enough, the paramagnetic behaviour of the crystal can be detected.[6] Paramagnetic resonance experiments carried out by Kittel[7] and others[8] on coloured sodium chloride have helped to elucidate the nature of *F*-centres and, in particular, to give a plausible picture of their wave function.

When crystals of sodium chloride are intimately mixed with borax glass, the curve of magnetic susceptibility against the concentration of sodium chloride is linear, whereas a non-linear plot is obtained if the same system is previously melted.[9]

The diamagnetic susceptibility of sodium chloride in aqueous solution, determined for various concentrations in the temperature range 0° to 50°C.,[2,3,10,11] differ but slightly from the value of the susceptibility in the solid state. This slight discrepancy has been interpreted as indicating that the diamagnetism of the ions is not strictly additive.[2] Though others have pointed out that the additivity principle is true only to a first approximation,[3,4] it is doubtful whether the difference between the diamagnetism of the solid and that in solution is properly attributable to this cause. Indeed, it has been stated[3] that the difference is less than the likely experimental error; and values of molar susceptibility typical of those that have been published are, for sodium chloride in aqueous solution and for solid sodium chloride, −30·8 × 10^{-6} and −30·1 × 10^{-6} c.g.s. units respectively.[2]

In accordance with Wiedemann's law, the diamagnetic susceptibility of sodium chloride in aqueous solution is a linear function of concentration up to

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25% by weight.[10]

Some observations have been made of the magnetic rotation of polarized light by aqueous sodium chloride solutions for wave-lengths of 5780, 5460 and 4360 A. at 0°C.,[12] and by aqueous solutions containing 1·486 g. equiv. l.$^{-1}$ of sodium chloride for wave-lengths of 6400, 5100 and 4358 A.[13] The molar magnetic rotation, M, varies slightly with concentration and also with the wave-length employed. For yellow light, M increases with increasing dilution. Okazaki,[14] who collected the available data on magneto-optical rotation of aqueous sodium chloride and other aqueous salt solutions, concluded that the decrease in molar magnetic rotation from $3{\cdot}77 \times 10^{-10}$ min. of arc cm.^{2} for dilute solution to $2{\cdot}47 \times 10^{-10}$ min. of arc cm.^{2} for concentrated solution can be interpreted as evidence for the 'existence of undissociated molecules in concentrated solutions'. In more modern terms it would be said that the results are explicable in terms of ion-association.

The value of M for polarized light of wave-length 5893 A., extrapolated to infinite dilution of sodium chloride, is $3{\cdot}66 \times 10^{-10}$ min. of arc cm.^{2} according to Okazaki.[15]

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Viscosity and Fluidity

Fused Salt and Fused Salt Mixtures.

From the data of Dantuma,[1] van Aubel[2] and Ipatov[3] it has been shown that in the temperature range 816° to 997°C. the specific volume of molten sodium chloride is related to the dynamic viscosity or its reciprocal, the fluidity. It is found[2] that Batchinski's law, that the specific volume of a non-associated liquid varies linearly with its fluidity, holds for the fused salt. One form of the Batchinski equation,[3]

$$\eta = \frac{C}{(v-\omega)},$$

where C and ω are constants whose values are respectively 0·000654 and 0·6080 for fused sodium chloride, and v is the specific volume measured at the same temperature as the dynamic viscosity, η, is obeyed to within ±2·0%.

At 700°C. the viscosity isotherm for the binary fused system NaCl-KCl is a straight line, whilst at 800°C. it is a smoothly concave curve.[4] In the system NaCl-CaCl$_2$ the isotherms are represented by fairly complex lines.[5] Initial additions of calcium chloride produce a small decrease in the viscosity of molten sodium chloride to a minimum value: further addition of calcium chloride increases the viscosity considerably and, at this stage, the isotherm is above the additivity line. A minimum in the viscosity isotherm is also found in the fused NaCl–BaCl$_2$ system.[5]

Studies have been made of the viscosity of two other fused salt systems containing sodium chloride: NaCl–PbCl$_2$[5] and NaCl–MgCl$_2$.[4] From the viscosity isotherms of the latter at 700° and 800°C., the existence of the compound NaMgCl$_3$ is considered possible. Numerical values of the viscosity are available for the binary systems mentioned at various temperatures and concentrations.[4,5]

Solutions of Sodium Chloride.

Table XXIV summarizes the results of various investigators up to 1928. F is the number of formula weights of sodium chloride dissolved in 1000 g. of water, and η is the viscosity in poises.

TABLE XXIV.- THE VISCOSITY OF AQUEOUS SOLUTIONS OF SODIUM CHLORIDE

F	Values of η at Various Temperatures (°C.)							
	0	10	18	25	40	60	80	100
0·1	1·004*	1·006*	1·0085+	1·009±	1·010*	1·012*	1·013*	1·013*
0·25	1·009*	1·016*	1·0205+	1·022±	1·026*	1·030*	1·031*	1·032*
0·5	1·020*	1·032*	1·0405+	1·046±	1·053*	1·060*	1·062*	1·065*
1·0	1·047*	1·071*	1·0840+	1·094±	1·108*	1·121*	1·127*	1·131*
2·0	1·147	1·173	1·192	1·205	1·229	1·249	1·26	1·26
3·0	1·282	1·312	1·329	1·341	1·365	1·39	1·40	1·405
4·0	1·450	1·481	1·498	1·509	1·524	1·54	1·55	1·555
5·0		1·692	1·700	1·706	1·713	1·72		

* ±0·005 + ±0·001 ± ±0·002

More precise determinations of relative viscosities have since been made on dilute solutions at 0° and 25°C.[7] The results are expressed in terms of the following equations, where η is the relative viscosity and c the concentration in g. equivalents/l:-

$$\eta^* = 1 + 0{\cdot}00670\sqrt{c} + 0{\cdot}07620c + 0{\cdot}01291c^2$$

at 25°C., the average deviation being 0·005% up to 1 N.; and

$$\eta^* = 1 + 0{\cdot}00448\sqrt{c} + 0{\cdot}018923c + 0{\cdot}025284c^2$$

at 0°C., the average deviation being 0·011% up to 2 N.

The fluidity of dilute sodium chloride solutions increases with increasing temperature, and it has been observed that the ratio of the temperature coefficient of fluidity and the temperature coefficient of conductance is roughly constant.[8] Solutions of sodium chloride show an increase of viscosity with rise of external pressure at all concentrations.[9] At a concentration of 3 N., a weak linear dependence of viscosity on pressure is obeyed. As the temperature rises the effect of external pressure decreases.[9]

A viscosity nomograph for sodium chloride solutions has been constructed.[10]

The addition of glycerol, sucrose, agar, or gelatin affects the viscosity of sodium chloride solutions;[11] and the product of the viscosity and ion-migration ($\eta\lambda_\infty$) always increases with increasing sucrose concentration.[12] This effect has been explained[12] by the suggestion that in sugar solutions aggregated molecules of sucrose and water are present, of size depending on temperature and concentration, which cause the viscosity to rise but do not affect ion-migration.

The viscosities of liquid ammonia solutions of sodium chloride have been determined from −30° to +30°C.[13]

Aqueous Solutions of Salt Mixtures Containing Sodium Chloride.

Measurements of the viscosities of aqueous binary mixtures of strong electrolytes, made by Chakravarti and Prasad[14] in 1940, provided the first experimental verification of the Onsager and Fuoss[15] limiting law which correlates relative viscosity and concentration in terms of the interionic attraction theory. The viscosities of mixed solutions of sodium chloride and barium chloride in the proportions 3:1, 1:1, and 1:3, and of magnesium chloride with sodium chloride in the proportions 4:1, 2:3 and 3:2, determined at 35°C., were found to fit the equation:

$$\eta/\eta_0 = 1 + A\sqrt{c} + BC$$

in accordance with the Onsager and Fuoss theory, A and B being constants and C the total concentration of electrolytes in g. mole l.$^{-1}$. The value for A for any mixture containing the salts in the ratio C_1/C_2 is given by the expression

$$A = xA_1 + (1 - x)A_2$$

where $x = c_1/(c_1 + c_2)$, is the fractional molar concentration of the first component, and A_1 and A_2 are the values of A for the first and second components respectively.[14] For mixtures of sodium chloride (first component) and barium chloride, A_1 is $1{\cdot}8 \times 10^{-2}$ and A_2 is $0{\cdot}6 \times 10^{-2}$. A more rigorous comparison[16] of the results of Chakravarti and Prasad with the theory of Onsager and Fuoss shows good agreement for sodium chloride–magnesium chloride aqueous mixtures, but for the barium chloride–sodium chloride system agreement is found only with mixtures containing more than 50% of sodium chloride.

The dynamic viscosities of aqueous solutions of pairs of electrolytes can be calculated by means of various additivity rules[17,18] provided the viscosities of the component solutions are known. Better agreement[19] is obtained between experimental values and those calculated from additivity formulae if the fluidity, rather than the viscosity, is used; e.g. for sodium chloride and barium chloride mixtures the fluidity, ϕ, of the homogeneous mixture is given by:

$$\phi = a\phi_1 + b\phi_2$$

a and b being volume concentrations and ϕ_1 and ϕ_2 the fluidities of the component solutions. This equation is superior to its viscosity analogue

$$\eta = a\eta_1 + b\eta_2.$$

Viscosity studies at 20°C. on aqueous solutions of sodium chloride and potassium chloride mixtures, and magnesium chloride and potassium chloride mixtures, showed that in the former system there is no evidence for the formation of molecular compounds of a higher order, unlike the latter where there is positive evidence for the existence of the compound $KCl,MgCl_2$.[20] The viscosities at several concentrations and temperatures of aqueous mixtures of sodium chloride and cobaltous chloride have been reported.[21]

Many observations have been made of the influence of the addition of sodium chloride on the viscosities of solutions of sugars, nucleic acids, soaps and polyelectrolytes. Data are available for aqueous solutions of the following: sucrose,[22] thymonucleate,[23] deoxyribonucleic acid,[24] sodium pectinate,[25] sodium dodecyl sulphate,[26] agar acid and its sodium salt,[27] polyacrylic acid[28] and sodium polyacrylate,[29] alginic acid[30] and sodium alginate,[31] and polymetaphosphate.[32] Data are also available for the following quaternary systems: sodium chloride–water–sodium caprylate and methyl, ethyl, propyl, butyl, amyl or hexyl alcohol;[33] sodium chloride–water–sodium laurate and methyl, propyl or butyl alcohol;[34] and sodium chloride–water–sodium stearate and methyl, propyl, *iso*propyl or butyl alcohol.[35]

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Diffusion

Numerous papers dealing with the measurements of the diffusion coefficient of sodium chloride in aqueous media by means of the conductimetric, Goüy (interference), and diaphragm-cell methods have appeared over the past twenty years.[1-17] The results obtained in this period largely supplant the considerable mass of data[18-24] obtained earlier.

In dilute solutions the diffusion coefficient, D, varies with concentration as shown in Table XXV, based on the paper by Hamed and Hildreth.[7] D^0, the diffusion coefficient at infinite dilution (= 1·610 × 10^5 cm.^{2} sec.$^{-1}$), was evaluated by means of the Nernst expression:[17]

$$D^0 = \frac{RT}{F^2} \; \frac{|Z_1|+|Z_2|}{|Z_1 Z_2|} \; \Lambda^0 t_1^0 t_2^0 \;\ldots\ldots\ldots\ldots(1)$$

in which Z_1 and Z_2 are the algebraic valencies of cation and anion respectively, t_1^0 and t_2^0 are the cation and anion transference numbers at infinite dilution, Λ^0 is the equivalent conductance at infinite dilution and R, T and F are the ideal gas constant, the absolute temperature and the Faraday respectively.

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TABLE XXV.- THE DIFFUSION COEFFICIENT OF DILUTE AQUEOUS SODIUM CHLORIDE SOLUTION AT 25°C.

C (mole l.$^{-1}$)	$D \times 10^5$ (cm.^{2} sec.$^{-1}$)
0·0	1·610
0·001	1·585
0·002	1·576
0·003	1·570
0·005	1·560
0·007	1·555
0·01	1·545

The theory of diffusion of single electrolytes in dilute solution is quite advanced; and the experimental data set out in Table XXV can be described excellently by the Onsager-Fuoss equation:[25]

$$D = (D^0 + \Delta_1 + \Delta_2)(1 + C \frac{d \ln y}{dc}) \quad \text{.........(2)}$$

where C is the molarity, y the activity coefficient on the molarity scale, and Δ_1 and Δ_2 are the first- and second-order electrophoretic terms respectively. The electrophoretic term is defined generally by:

$$\Delta_n = \frac{\boldsymbol{k}TA_n\,(Z_1^n t_2^o + Z_2^n t_1^o)^2}{a^n |Z_1 Z_2|} \quad \text{..........(3)}$$

$\boldsymbol{k}$ is Boltzmann's constant, a the mean diameter of the ions in A., and the coefficient A_n is a function of temperature, dielectric constant and viscosity of the solvent. (Numerical values of A_n have been tabulated for aqueous solutions).[17] The value of a for sodium chloride solutions is 3·97 A.[17]

The diffusion coefficients at higher concentration, together with values of other relevant parameters and combinations of parameters are appended.[17]

TABLE XXVI.- DIFFUSION COEFFICIENTS OF SODIUM CHLORIDE SOLUTIONS AT 25°C.

m	$D_{obs.}$	Δ_1	Δ_2	$1 + m\frac{d \ln y}{dm}$	η/η^0	$f(D)$	$f(D)\eta/\eta^0$
0·0	1·610	0	0	1·000	1·000	(1·000)	(1·000)
0·01	1·547	−0·003	+0·009	0·955	1·001	1·001	1·002
0·05	1·506	−0·006	+0·024	0·927	1·004	0·997	1·001
0·1	1·484	−0·008	+0·032	0·917	1·009	0·989	0·998
0·2	1·478	−0·010	+0·040	0·914	1·018	0·985	1·002
0·3	1·477	−0·011	+0·043	0·915	1·027	0·982	1·009
0·5	1·474	−0·013	+0·049	0·927	1·046	0·965	1·009
0·7	1·475	−0·014	+0·050	0·946	1·065	0·946	1·007
1·0	1·482	−0·015	+0·052	0·970	1·094	0·927	1·014
1·5	1·494	−0·016	+0·052	1·031	1·147	0·879	1·008
2·0	1·511	−0·017	+0·051	1·096	1·205	0·838	1·010
3·0	1·538	−0·018	+0·049	1·245	1·341	0·752	1·008
4·0	1·567	−0·019	+0·047	1·410	1·509	0·678	1·023

In Table XXVI m is the molality, y the mean activity coefficient on the molality scale, η the bulk viscosity of the solution, η^0 the viscosity of pure water, and $f(D)$ is defined by:

$$f(D) = D_{obs.} / [(D^0 + \Delta_1 + \Delta_2)(1 + m \frac{d \ln y}{dm})] \quad \text{.........(4)}$$

It can be shown[17] that:

$$D = (D^0 + \Delta_1 + \Delta_2)\left(1 + m\frac{d\ln\gamma}{dm}\right)\left[1 + 0{\cdot}036\,m\left(\frac{D^*_{H_2O}}{D^0} - n\right)\right]\frac{\eta^0}{\eta}\ldots\ldots\ldots(5)$$

where $D^*_{H_2O}$ is the self-diffusion coefficient of pure water, and n is the hydration number. From the data given in Table XXVI, the value of n obtained using the combined equation:

$$\frac{\eta}{\eta^0}f(D) = 1 + 0{\cdot}036\,m\left(\frac{D^*_{H_2O}}{D^0} - n\right)\ldots\ldots\ldots(6)$$

is 1·1. The latter is the hydration number of both the sodium and chloride ions; and when, in turn, it is used as the value of n in equation (5) the calculated diffusion coefficients so produced deviate by less than 0·2% from the observed diffusion coefficients in the concentration range 0 to 4·0 molal.[17]

Very recently,[17] the ratios D/D^0, where D is now the diffusion coefficient of an added tracer ion and D^0 is the self-diffusion coefficient of that ion at infinite dilution, have been determined for both the sodium and chloride ions in sodium chloride as supporting electrolyte. The results are tabulated in Table XXVII.[25a]

TABLE XXVII.- DIFFUSION OF SODIUM AND CHLORIDE IONS IN SODIUM CHLORIDE SOLUTIONS

	Concentration of Supporting Electrolyte (mole $l.^{-1}$)					
	0·1	0·5	1·0	2·0	3·0	4·0
$\frac{D}{D^0}$ for Na+	$0{\cdot}97_4$	$0{\cdot}95_9$	$0{\cdot}92_5$	$0{\cdot}84_9$	$0{\cdot}77_2$	$0{\cdot}69_7$
$\frac{D}{D^0}$ for Cl−	$0{\cdot}96_1$	$0{\cdot}91_2$	$0{\cdot}87_2$	$0{\cdot}79_4$	$0{\cdot}71_3$	$0{\cdot}67_1$

The respective values of D^0 for the sodium ion and chloride ion are 1·333 and 2·045 × 10^{-5} cm.^{2} sec.$^{-1}$.

There is very little information available on diffusion of sodium chloride in mixtures with other simple electrolytes,[17] but the rate of inter-diffusion of hydrochloric acid and sodium hydroxide in the presence of sodium chloride has been studied.[26]

In contrast to the situation with regard to mixtures of electrolytes, the influence on the diffusion of sodium chloride of the presence of non-electrolytes and colloidal electrolytes has been much studied. Even though the mechanism and the theory of the *rọle* of electrolytes in the flocculation and coagulation of sols is not yet fully understood,[27] a good deal of empirical knowledge of several systems has been garnered. The *role* of diffusion of sodium chloride in the coagulation of, or the penetration into, the following substances has been studied: arsenious sulphide[28,29] and antimonyl sulphide[28] sols, sodium humate,[30] iron oxide sols,[31] bentonite sols,[32] sodium dodecyl sulphate solutions,[33] hexadecyl pyridinium chloride,[34] agar gel,[35] gelatin gels[36-40] and a sulphur sol.[41]

Diffusion in Solid Sodium Chloride.

Detailed studies of the electrical conductance of solid sodium chloride have demonstrated that the current carrier is the sodium ion. There is strong theoretical evidence to suggest that the mechanism of this conduction depends on migration of cation vacancies (see page 837). If diffusion of sodium ions and their migration in an electric field proceed by the same mechanisms then the Einstein relation:[42,43]

$$\frac{v}{D} = \frac{e}{kT}$$

should hold. Here, D is the self-diffusion coefficient of the sodium ions, v

its rate of movement under unit field (*i.e.* the sodium ion mobility), *e* the electronic charge and *k* the Boltzmann constant. Above temperatures of approximately 550°C. there is sound evidence to show that this relation is obeyed, the self-diffusion coefficient of the sodium ion measured directly being in close agreement with that calculated from the measured electrical conductance.[44,45] The relation is not obeyed at low temperatures (*i.e.* less than 550°C.), and the reasons for this are precisely those that explain the variability of the electrical conductance of sodium chloride over a similar range of temperature (see page 836). In this connection, it may be significant that the self-diffusion coefficient of the sodium ion in sodium chloride is altered by heat treatment[46,47] and is decreased if the crystal is exposed to *X*-rays during the diffusion process.[48] This latter effect is observed only at temperatures less than 550°C.[48]

Actual values of the diffusion coefficient of the sodium ion at different temperatures have been published.[43,48,49] In Table XXVIII are listed the values obtained by Murin[49] and Luv'e using β-active ^{24}Na.

TABLE XXVIII.- SELF-DIFFUSION COEFFICIENT OF THE SODIUM ION IN SODIUM CHLORIDE

Temp.°C.	$10^{10} \times D$ (cm.^{2} sec.$^{-1}$)
650	7·0
665	8·0
680	14·0

Chemla[50] studied the self-diffusion of the chloride ion in a single crystal of sodium chloride using radioactive ^{36}Cl and his results are summarized in Table XXIX.

TABLE XXIX.- THE SELF-DIFFUSION COEFFICIENT OF THE CHLORIDE ION IN SODIUM CHLORIDE

Temp.°C.	$10^{10} \times D$ (cm.^{2} sec.$^{-1}$)
650	0·725
681	2·84
703	6·76
735	16·7
762	25·2

Chemla[51-55] has also studied the diffusion of foreign ions in sodium chloride. For the radioactive isotopes ^{35}S and ^{32}P, which are the products of the reactions ^{35}Cl (n,p) and ^{35}Cl (n,α) respectively when sodium chloride is subjected to neutron bombardment, the values of the activation energy, W, in the equation:

$$D = D^0 \exp.(-W/RT) \qquad \text{..........(7)}$$

are 1·90 and 3·30 e.V. respectively.[51-53] In the temperature range 653°–775°C., the ratio of the electrical mobility to the diffusion coefficient for ^{35}S is approximately 300 e.s.u. and varies little with temperature.[53] The diffusion of the ^{137}Cs, ^{42}K, ^{86}Rb and ^{110}Ag ions, on the other hand, all conform to the Einstein relation from 575° to 760°C.[54,55]

The volume diffusion of helium through high-purity sodium chloride between 25° and 147°C. is described by equation (7) with $D_c^0 = 2{\cdot}8 \times 10^{-2}$ cm.^{2} sec.$^{-1}$ and $W = 18{\cdot}6 \pm 1{\cdot}4$ kg.-cal. mole^{-1}.[56] At higher temperatures (500° to 650°C.) equation (7) is still valid; and when the plot of log D against the reciprocal of the absolute temperature is extrapolated it yields values of D at 80° and 40°C. which are respectively $4{\cdot}0 \times 10^{-17}$ and $3{\cdot}2 \times 10^{-19}$ cm.^{2} sec.$^{-1}$.[57]

Diffusion of Sodium Chloride in the Vapour Phase.

The coefficient of diffusion of sodium chloride and other alkali halides in

Bunsen flames is given by the equation:

$$D = \frac{rV}{2}\left\{\left(\frac{dx}{dr}\right) - 1\right\}\text{..........}(8)$$

where r is the distance from the bead of salt held in a loop of platinum inside the flame to any point, x the vertical distance of this point above the bead, and V the vertical velocity of the flame gases.[58] For sodium chloride this diffusion coefficient is 19·0 ± 1·9 at a flame temperature of 1436°C.[58]

Thermal Diffusion.

Clusius and Dickel,[59] in developing the technique of separation by thermal diffusion, gave an elegant demonstration using 0·1 N. aqueous sodium chloride. Using a tin vessel 20 × 1 mm. in cross section and 1·5 m. long, with the top heated by steam or hot water, the bottom cooled by cold water and the slope varied to give optimum conditions, they obtained, in 4 hr. with a temperature difference of 80°C. at the lower (heavy) side a 3·6-fold concentration.[59] Another experiment[60] employing the Clusius separation tube yielded a value for the thermal diffusion coefficient, α, of sodium chloride which was about one-third that of the normal diffusion coefficient.

Theoretical formulae describing thermal diffusion in mixed electrolyte solutions have been applied to the sodium chloride–hydrochloric acid solution, sodium chloride–ammonium chloride solution, and sodium chloride–sodium hydroxide solution systems.[61] A detailed analysis of thermal diffusion potentials of sodium chloride solutions has been made.[62]

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Solubility

Although the present state of solution theory does not permit the calculation of the solubility of electrolytes from the fundamental properties of the constituents involved, many useful rules and equations have, nevertheless, been established. Moreover, several reasonably successful attempts have been made to correlate the solubility of electrolytes with such properties as parachor, dielectric constant and ionic radius. For sodium chloride, the extensive solubility data that have been accumulated, even for the less commonly used solvents, are of value, not only in elucidating the structure and thermodynamics of ionic solutions, but also practically.

Solubility of Sodium Chloride in Water.

Table XXX lists[1] the solubilities of rock salt at ordinary temperatures.

TABLE XXX.- SOLUBILITY OF SODIUM CHLORIDE IN WATER[1]

Temp.°C.	g. NaCl per 100 g. H_2O	g. NaCl per 100 g. soln.	Temp.°C.	g. NaCl per 100 g. H_2O	g. NaCl per 100 g. soln.
0	35·63	26·28	70	37·51	27·27
10	35·69	26·29	80	38·00	27·54
20	35·82	26·37	90	38·52	27·80
30	36·03	26·49	100	39·12	28·12
40	36·32	26·65	140	42·10	29·63
50	36·67	26·83	160	43·60	30·37
60	37·06	27·04	180	44·90	30·98

The data in Table XXXI enable the ice-curve for aqueous solutions of sodium chloride to be drawn and show that there is a eutectic temperature at 21·1°C., where the dihydrate, $NaCl,2H_2O$, separates out.

TABLE XXXI.- DATA FROM THE ICE-CURVE OF SODIUM CHLORIDE[1-1 d]

Temp.°C.	g. NaCl per 100 g. satd. soln.	Solid Phase
−21·1	23·0	Ice + $NaCl,2H_2O$
−15	24·25	$NaCl,2H_2O$
−10	25·0	$NaCl,2H_2O$
−5	25·6	$NaCl,2H_2O$
+0·1	26·3	$NaCl,2H_2O$ + NaCl
10·0	26·34	$NaCl,2H_2O$ + NaCl
15·0	26·34	$NaCl,2H_2O$ + NaCl
20	26·40	NaCl
25	26·406	NaCl
30	26·52	NaCl
40	26·67	NaCl
60	27·07	NaCl
80	27·55	NaCl
100	28·15	NaCl

A more recent study[2] of the properties and conditions for the formation of $NaCl,2H_2O$ has established that the eutectic temperature is −21·2°C., and that from the saturated solution the dihydrate crystallizes between this temperature and +0·15°C., the new value for the melting point of the dihydrate. The presence of other salts, notably magnesium chloride, lowers the dihydrate crystallization temperature; and the cryohydrate formed at temperatures below −21·2°C. contains 36% of $NaCl,2H_2O$ and 64% of ice. The specific gravity of $NaCl,2H_2O$ is 1·61, and its vapour pressure 3·48 and 0·70 mm. Hg at 0·15° and −21·2°C. respectively.[2]

The solubility of sodium chloride in water increases with increasing temperature as shown in Table XXXII.

TABLE XXXII.- SOLUBILITY OF SODIUM CHLORIDE IN WATER AT TEMPERATURES ABOVE 100°C.[1 d,3]

Temp.°C.	g. NaCl per 100 g. satd. soln.	Temp.°C.	g. NaCl per 100 g. satd. soln.
100	28·4	300	37·2
150	29·7	350	41·7
200	31·6	400	46·4
250	34·0	450	50·8

The large body of quantitative data on the phase behaviour of the sodium chloride–water system at temperatures above 374°C.[4,5] indicates that solvation of the solute molecules in the vapour solution is quite extensive: these data also reveal that the partial molal volumes of sodium chloride in steam are among the largest ever recorded (approximately −2·1).[4]

With increasing external pressure the solubility of sodium chloride is enhanced, and this effect has been correlated qualitatively with the types of cohesive forces in the pure components and in the solution,[6] and quantitatively with vapour pressure, density and compressibility.[7] The quantitative approach has proved successful, the solubilities calculated for sodium chloride at 18° and 25°C. under pressures of up to 10,000 atm. being in satisfactory agreement with those determined experimentally.[7] Adams and Hall[8] have compared the solubility measurements made prior to 1930 under pressures up to about 4000 atm. and at ordinary temperature with those made using their special high-pressure conductance cell. The isobaric solubility of sodium chloride in superheated steam, which has been investigated under pressures of 180 to 200 atm. and at different steam temperatures, has a minimum of 23 mg. per kg. of steam at 500°C. and 180 atm.[9]

The temperature of incongruent melting of $NaCl,2H_2O$, which is +0·15°C. under 1 atm. pressure, increases steadily with increasing pressure up to about 9500 atm., where its value is 25·8°C. and decreases from that pressure to 12000 atm.[10]

Whereas 35·9 g. of sodium chloride will dissolve in 100 g. of ordinary water at 25°C., only 30·5 g. will dissolve in water containing 92% of deuterium oxide, a difference of nearly 15%.[11] If S_n is the number of moles of sodium chloride that are dissolved in 55·51 moles of a water mixture, and n is the mole fraction of heavy water, then the linear relation: $S_n = 6{\cdot}145 - 0{\cdot}334n$ holds within ±0·1%.[12]

Solubility of Sodium Chloride in Anhydrous Inorganic Solvents.

In pure hydrogen peroxide the solubility data for sodium chloride, determined by the freezing point method, are as given in Table XXXIII.

TABLE XXXIII.- SOLUBILITY OF SODIUM CHLORIDE IN PURE HYDROGEN PEROXIDE[12a]

F.p., t°	g. NaCl per 100 g. Satd. Soln.
−2·37	1·08
−3·62	3·14
−5·07	5·42
−7·67	8·61
−10·7	11·61
−10·37	15·63

Many determinations have been made of the solubility of sodium chloride in liquid ammonia at different temperatures.[13-23] The results are summarized in Table XXXIV.

TABLE XXXIV.- SOLUBILITY OF SODIUM CHLORIDE IN LIQUID AMMONIA[13,15,16,23]

Temp. °C.	g. NaCl per 100 g. Sat. Soln.	Solid Phase
−76·3	0·0	NH_3
−76·6	0·28	$NH_3 + NaCl,5NH_3$
−70·0	0·4	$NaCl,5NH_3$
−60·0	0·55	$NaCl,5NH_3$
−50	1·15	$NaCl,5NH_3$
−40	2·10	$NaCl,5NH_3$
−30	4·0	$NaCl,5NH_3$
−20	7·5	$NaCl,5NH_3$
−15	10·6	$NaCl,5NH_3$
−12·5	12·6	$NaCl,5NH_3$
−10	14·5	$NaCl,5NH_3$
−8·5	16·3*	$NaCl,5NH_3$
−9·5	15·4	$NaCl,5NH_3$
−11·5	16·3*	$NaCl,5NH_3 + NaCl$
−5·0	13·4	NaCl
0·0	11·5	NaCl

continued on following page

TABLE XXXIV continued

Temp.°C.	g. NaCl per 100 g. Sat. Soln.	Solid Phase
+10	7·85	NaCl
20	5·3	NaCl
30	3·2	NaCl
40	2·0	NaCl
45	1·6	NaCl

* Metastable

The only ammoniate formed is $NaCl,5NH_3$, which has a solubility maximum at −9·5°C. and crystallizes in long needles. The solubility in liquid ammonia is greatly increased if sodamide is added.[21]

Unlike covalent compounds with molecular lattices, which are quite soluble, ionic compounds are only slightly soluble in liquid sulphur dioxide.[24] At 25°C., 0·00040 g. of sodium chloride will dissolve in 100 g. of saturated solution.[24] This figure is greater than the solubility of lithium chloride (0·00062) and less than that of potassium chloride (0·0126) under identical conditions. At 50°C., under pressure, sodium chloride dissolves in liquid sulphur dioxide to an extent less than 0·001%.[24]

The solubility of sodium chloride in anhydrous liquid phosphorus oxychloride at 20°C. is 0·31 $g.l.^{-1}$ compared with 0·05 and 0·60 $g.l.^{-1}$ for lithium chloride and potassium chloride respectively.[25]

In common with all other alkali and alkaline earth halides, sodium chloride, when dissolved in liquid hydrogen fluoride, reacts to give the corresponding hydrogen halide which is liberated.[26]

Solubility of Sodium Chloride in Aqueous, Inorganic Mixtures.

Table XXXV gives the solubility of sodium chloride in aqueous ammonia.

TABLE XXXV.- SOLUBILITY OF SODIUM CHLORIDE IN AQUEOUS AMMONIA AT 30°C.[26a]

d_{30} of Satd. Soln.	g. per 1000c.c.of Satd. Soln.	
	NH_3	NaCl
1·1735	29·535	293·38
1·1656	40·655	292·5
1·160	47·26	289·7
1·1494	60·78	286·5
1·1406	72·07	283·38
1·1395	72·715	283·06
1·1301	81·855	277·49
1·1205	97·49	270·57

Solubility curves for sodium chloride in mixtures of ammonia and water containing 0–100% of water at temperatures between −40° and +25°C. have been published.[27] If x_0 is the solubility of sodium chloride in 100 g. of water, and x the solubility in an aqueous solution of y g. of ammonia in 100 g. of water, the solubility is given by:[28]

$$\log x = \log x_0 + k(A - a)y \text{..........(1)}$$

where a is the water activity coefficient at the temperature t, and the two constants k and A are given by:

$$k = 0{\cdot}01171 - 0{\cdot}000542t \quad \text{and} \quad A = 0{\cdot}840 - \frac{0{\cdot}0023}{k}$$

The solubilities given by this formula agree within ±2·5% with the experimental values.[28]

In aqueous solutions of hydrochloric acid the solubility increases with decreasing concentration of hydrochloric acid[1,29,30] as shown in Table XXXVI.

TABLE XXXVI.- SOLUBILITY OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID AT 25°C.[30a]

G. mols. per litre satd. soln.		density of satd. soln.
HCl	NaCl	
0·0	5·4325	1·1981
0·503	4·880	1·1867
0·886	4·483	1·1781
2·265	3·149	1·1511
3·185	2·310	1·1352
3·487	2·079	1·1319
3·830	1·797	1·1282
4·500	1·333	1·1200
5·253	0·907	1·1160
6·101	0·544	1·1158
7·073	0·293	1·1213
7·976	0·158	1·1302
9·236	0·091	1·1458
13·41	0·017	1·1970

Owing to hydration of the acid, sodium chloride is practically insoluble in a solution having the molecular composition $HCl:4H_2O$.[31] Akhumov and Spiro[32] have derived theoretically an equation

$$\log \phi = a + b \log c \text{..........}(2)$$

which relates the concentration, c, of a salt MR_n in an aqueous solution of an acid HR to the so-called reduced equilibrium constant ϕ, a and b being constants. The reduced equilibrium constant is defined by the relation: $\phi = K_c/K_a$, where K_c is the equilibrium constant expressed in terms of concentrations, and K_a that in terms of activities. It is thus a measure of the non-ideality of the solution, and its evaluation involves the knowledge of activity coefficients. Equation (2) is substantiated by the fact that it describes the solubilities of sodium chloride at 30°C., magnesium chloride at 0° and 25°C., and mixtures of sodium chloride and potassium chloride at 25°C. all in aqueous solutions of hydrochloric acid.[32]

Solubility data for sodium chloride in aqueous sodium hydroxide solutions are given in Tables XXXVII and XXXVIII.

TABLE XXXVII.- SOLUBILITY OF SODIUM CHLORIDE IN AQUEOUS SODIUM HYDROXIDE AT 25°C.[1,32a]

G. mols. per 1000 g. H_2O		G. mols. per 1000 g. H_2O		G. mols. per 1000 g. H_2O	
NaOH	NaCl	NaOH	NaCl	NaOH	NaCl
0·920	5·613	8·031	2·173	16·25	0·580
1·858	5·048	8·876	1·956	17·32	0·533
2·714	4·672	9·824	1·558	17·83	0·492
3·070	4·486	11·437	1·280	19·30	0·451
3·812	4·048	11·582	1·253	20·30	0·421
4·798	3·610	12·350	1·074	21·05	0·396
5·721	3·206	13·27	0·940	21·94	0·371
6·688	2·635	14·38	0·781	22·82	0·356
7·141	2·442	15·20	0·714	23·68	0·346

TABLE XXXVIII.- SOLUBILITY OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE AT VARIOUS TEMPERATURES[1,32b]

g. NaOH per 1000 g. sat. soln.	g. NaCl dissolved per 100 g. sat. soln. at 0° C.	50° C.	120° C.
5	21·9	22·4	24·6
10	17·8	18·3	20·4
15	14·1	14·7	16·8
20	10·5	11·1	13·3
25	7·2	8·0	10·5
30	4·3	5·3	8·2
35	2·2	3·4	6·5
40	-	2·3	5·2
45	-	1·8	4·4
50	-	1·5	3·8
55	-	1·3	3·6
60	-	-	3·8
65	-	-	4·1
70	-	-	4·5

Solubility of Sodium Chloride in Aqueous Solutions Containing One or More Electrolytes.

Comprehensive tables of solubilities of sodium chloride in aqueous electrolyte solutions are given by Seidell[1] and in several original papers. Solubility data are available for the following electrolyte solutions: the chloride,[1,33] nitrate,[1,33] sulphate,[1] chromate,[1] permanganate[1] and dichromate[1] of potassium; the chlorate,[1,34] perchlorate,[1] dichromate,[1] bicarbonate,[1] iodate,[1,35] nitrate,[1] sulphate,[1,36] thiosulphate,[1] fluoride,[1] iodide[1,37] and bromide[38] of sodium; the sulphate[33] and chloride[1,33,39] of the ammonium ion; the chlorides of silver,[40] mercuric mercury,[33] strontium,[33] barium,[33] plumbous lead[1] and magnesium;[1] calcium oxalate;[41] manganous iodate;[42] and boric acid.[43]

Virtually all attempts to derive rules describing the solubility of one solute in the presence of another have been restricted to solutions in which the solutes have a common ion. The equation:

$$S_0 - S = KX^m \text{..........(3)}$$

for the solubility of a salt in a solution having a common ion holds only if the salts in question separate out in crystals containing no water of crystallization, form no mixed crystals and yield no double salts.[44] Here, S_0 is the solubility of the saturating salt in unit volume of its own aqueous solution, S the quantity of saturating salt in unit volume of solution in the presence of a quantity X of added salt, and m and K are constants. K depends on the salt pair and varies with the temperature, while m depends only on the saturating salt.

For the solubility of a salt AB in a solution of a salt AC the equation:

$$N_x = K_1(1 + a)^n + K_2 \text{..........(4)}$$

has been derived,[45] in which N_x is the mole fraction of the common ion A, a is the ratio of the concentrations in gram equivalents of C and B, and K_1, K_2, and n are constants. For the solubility of a salt AB in a solution of AC and AD the equation becomes:

$$N_x = K_1(1 + a + b)^n \text{..........(5)}$$

where b is the ratio of the number of gram equivalents of D to those of B, and n is a function of b/a but is independent of $(a + b)$.[45,46] This equation has been confirmed by experiments on the solubility of sodium chloride in solutions of sodium iodide and sodium nitrate, sodium bromide and sodium nitrate,

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potassium chloride and magnesium chloride, potassium chloride and calcium chloride, and ammonium chloride and calcium chloride.[45]

Akhumov and Spiro,[32,47,48] whose introduction of the concept of reduced equilibrium constant, ϕ, has already been mentioned (see equation (2)), have treated three component systems such as sodium chloride–potassium chloride–water, in which the solution is unsaturated with respect to one component as a new solvent for the component with respect to which the solution is saturated. In such a system, if the concentration of one component is held constant, the solubility of the other component varies exponentially with the temperature. At constant temperature, log ϕ is proportional to the logarithm of the component with respect to which the solution is saturated.[47] Graphical methods of solving this equation have been given: the equation can be solved algebraically only when it is not higher than fourth order.[48]

Solubility of Sodium Chloride in Anhydrous Organic Solvents.

As is shown in Table XXXIX sodium chloride is only very slightly soluble in the common aliphatic monohydric alcohols.[1,49–51,51a]

TABLE XXXIX.- SOLUBILITY OF SODIUM CHLORIDE IN SEVERAL ALCOHOLS AT 25°C.[51a]

Alcohol	g. NaCl per 100 g. of solvent	Density of Satd. Soln.
Methanol	1·401	0·7977
Ethanol	0·0649	0·7857
1-Propanol	0·0124	0·8000
1-Butanol	0·0050	0·8058
2-Propanol	0·0027	0·7809
2-Methyl-1-propanol	0·0020	0·7980
1-Pentanol	0·00177	0·8099
2-Butanol	0·00047	0·8022

Tabular and graphical data for the solubility of sodium chloride in ethylene glycol at 30°C. are also available.[52]

In anhydrous acetic acid the solubility of sodium chloride, which is very small at room temperature, increases slightly with increasing temperature as seen from Table XL.[1,53]

TABLE XL.- SOLUBILITY OF SODIUM CHLORIDE IN ANHYDROUS ACETIC ACID[53]

Temp. °C.	Mols. NaCl per 100 mols. satd. soln.
30	0·076
41	0·081
45	0·085
54	0·097
60	0·105
68	0·115
76	0·130
84	0·145
92	0·166

The solubility of sodium chloride in formic acid has recently been accurately measured and compared with the values given in the older literature.[50] The solubilities in acetone[54,55] and acetonitrile[50] have also been recorded.

The presence of other salts may modify the solubility of sodium chloride in non-aqueous solvents in much the same way as they modify its solubility in water. In the presence of sodium nitrate, for instance, the solubility of sodium chloride in acetone and 2-propanol is depressed, presumably owing to the influence of the common ion. However, if the second salt has no common ion, e.g. ammonium nitrate, the solubility is increased.[56] The solubility depression in these solvents is about one quarter that in water, while the increase on addition of a salt without a common ion is about four times as great as that in water. Nevertheless, both these effects are much smaller than those predicted by the Debye–Hückel inter-ionic attraction theory, owing probably to the incomplete dissociation of the salts attributable to the rather low dielectric constants of these solvents.

Two attempts have been made to correlate the solubility of alkali halides with the dielectric constant of the solvent.[55,57] The more satisfactory of these yields the following approximate equation:

$$\log\left(\frac{S_{\mathrm{I}}}{S_{\mathrm{II}}}\right) = a\left\{\frac{1}{D_{\mathrm{I}}} - \frac{1}{D_{\mathrm{II}}}\right\}\ldots\ldots..(6)$$

where S_{I} and S_{II} are the solubilities in solvents I and II, the dielectric constants of which are D_{I} and D_{II} respectively, and a is a constant. This equation, which may also be written as

$$\log S = \frac{a}{D} + b\ldots\ldots\ldots.(7)$$

(where b is another constant), yields as a further approximation $\log SD^{a} =$ constant. On comparing this with Walden's rule, $SD^{1/3}$ = constant, $a = 1/3$. Equation (7) describes satisfactorily the solubility of sodium chloride, potassium bromide, rubidium chloride and other Group I and Group II metal salts in water, methanol, ethanol, propanol and butanol.[57]

Solubility of Sodium Chloride in Aqueous Organic Mixtures.

Tables XLI and XLII list the solubilities of sodium chloride in aqueous methanol and aqueous ethanol respectively.

TABLE XLI.- SOLUBILITY OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS OF METHYL ALCOHOL AT 25°C.[57a]

Wt.-% CH_3OH in solvent	g. mols. NaCl per 1000 g. solvent
0·0	6·162
10·59	5·038
20·49	4·096
30·16	3·273
39·80	2·552
50·65	1·896
60·10	1·328
70·83	0·8656
80·45	0·5544
89·29	0·3685
100·00	0·2367

TABLE XLII.- SOLUBILITY OF SODIUM CHLORIDE IN AQUEOUS ETHYL ALCOHOL[57a]

Temp. °C.	Wt.-% C_2H_3OH in solvent	g. NaCl per 100 g. solvent
20	50·0	9·8
25	20·4	22·86
25	42·5	12·84
25	67·9	4·07
100	50·0	12·1

Data for the solubility in many other aqueous alcohol solutions are available.[1]

The solubility of sodium chloride in a 50% aqueous ethanol solution at 20°C. is increased appreciably by the addition of either benzene, carbon tetrachloride or methyl salicylate.[58] This 'salting in' process is explicable in terms of the solvation of the added organic species by the alcohol which increases the amount of free water available as solvent for the electrolyte.

For the general ternary system S-L_1-L_2, in which the solubility of a solid substance, S, in a binary mixed solvent, $L_1 + L_2$, is considered, and, in particular, for the sodium chloride–ethanol–water system, Akhumov[59] has deduced theoretically the equation:

$$Y = Y_1(1 - X)^{n_1} + Y_2(X)^{n_2}\ldots\ldots\ldots(8)$$

Here, Y is the isothermal solubility of S in the binary mixture $L_1 + L_2$, Y_1 and Y_2 are the separate solubilities of S in the binary system S-L_1 and S-L_2, X is the number of moles of L_2 in the binary solvent, and the exponents n_1 and n_2 determine the processes of solvation between the components of the mixed solvents L_1 and L_2 in the presence of the third component S in the solution. Akhumov[59] has also derived an equation which can be utilized for the calculation of the number of moles of water that hydrate the alcohol in water–alcohol solutions.

Seidell[1] gives data on the equilibria in the sodium chloride–butyric acid–water, sodium chloride–*iso*butyric acid–water and sodium chloride–tartaric acid systems, while similar data have been given[60] for the sodium chloride–acetic acid–water system.

The solubility of diethyl ether in aqueous sodium chloride solutions decreases as the sodium chloride concentration increases.[61,62] At 25°C. the amount of ether contained in 100 g. of solution varies from 6·05 g. in pure water to 0·31 g. in water containing 25 g. of sodium chloride per 100 g. of solution.[61] Except in dilute solutions, the Setchnekov equation:

$$\log\left(\frac{S_0}{S}\right) = kc\ldots\ldots\ldots(9)$$

is obeyed, where S is the amount of ether contained in 100 g. of solution, S_0 the solubility of ether in pure water, and c is the number of grams of sodium chloride per 100 g. of solution.

The solubility of sodium chloride in glucose solutions, which has been much studied,[1,63] is shown in Table XLIII.

TABLE XLIII.- EQUILIBRIUM IN THE SYSTEM SODIUM CHLORIDE GLUCOSE AND WATER AT 24°C.[1,63a]

g. per 100 g. satd. soln.		Solid Phase
$C_6H_{12}O_6$	NaCl	NaCl
0·0	26·46	NaCl
2·84	25·87	NaCl
5·21	25·28	NaCl
9·90	24·10	NaCl
13·09	23·38	NaCl
19·77	21·90	NaCl
23·87	20·83	NaCl
27·81	19·87	NaCl
29·47	19·50	NaCl + NaCl,2[$C_6H_{12}O_6$]H_2O
31·70	18·10	NaCl,2[$C_6H_{12}O_6$],H_2O
33·74	16·87	NaCl,2[$C_6H_{12}O_6$],H_2O
34·92	15·98	NaCl,2[$C_6H_{12}O_6$],H_2O

continued on following page

TABLE XLIII.- continued

g. per 100 g. satd. soln.		Solid Phase
$C_6H_{12}O_6$	NaCl	NaCl
36·90	14·50	$NaCl,2[C_6H_{12}O_6],H_2O$
38·67	13·61	$NaCl,2[C_6H_{12}O_6],H_2O$
44·05	10·95	$NaCl,2[C_6H_{12}O_6],H_2O$
47·35	9·57	$NaCl + C_6H_{12}O_6,H_2O$
47·23	8·28	$C_6H_{12}O_6,H_2O$
47·73	7·65	$C_6H_{12}O_6,H_2O$
47·74	6·97	$C_6H_{12}O_6,H_2O$
48·08	5·60	$C_6H_{12}O_6,H_2O$
48·55	2·49	$C_6H_{12}O_6,H_2O$
48·68	0·00	$C_6H_{12}O_6,H_2O$

Data on the solubility of organic substances in aqueous sodium chloride solutions are available for the following systems: sodium chloride-urea-water,[1] sodium chloride-dioxan-water,[1] sodium chloride-formamide-water,[1] sodium chloride-ethyl urethane-water,[1] sodium chloride-acetone-water,[1] sodium chloride-methyl ethyl ketone-water,[1] sodium chloride-ethyl acetate-water,[64] sodium chloride-N-chloroacetanilide-water[65] and sodium chloride-Orange II-water.[66]

Solubility of Gases in Sodium Chloride Solutions.

Carbon dioxide is less soluble in sodium chloride solutions than in pure water, and in nearly saturated brine the solubility is only 30% of that in pure water.[67] Chlorine behaves similarly, and its solubility decreases markedly with increasing concentration of the brine, e.g. at 20°C. and 762 mm. Hg, 1·577 volumes of chlorine are dissolved in 0·777% sodium chloride solution, while only 0·719 volumes are dissolved in a 3·597% solution.[68] The empirical formula first enunciated by Gordon[69]

$$\frac{(a' - a)}{M^{2/3}} = K \quad \ldots\ldots\ldots\ldots (10)$$

where a is the absorption coefficient of the gas in pure water (volume dissolved x 760/pressure = a'), a the absorption coefficient in the electrolyte solution and K a constant, adequately expresses the solubility of chlorine in brine.[68]

The solubility data for phosphine fit the Setchnekov equation (equation (9)).[70] The solubilities of both iodine[71,72] and bromine[72] in brine are known.

Velocity of Solution.

Following the early work on the measurement of the rate of solution of rock salt in various solvents,[73-77] several papers dealing with the experimental and theoretical aspects of the subject have been published[78-84] which have engendered acceptable, general theories for the kinetics and mechanism of solute dissolution. When the rate-determining step is the surface process

$$\frac{dx}{dt} = aA(C_S - C_y) \quad \ldots\ldots\ldots\ldots (11)$$

where a is the rate constant, A the surface area of the dissolving crystals, C_S the solubility, C_y the concentration in the boundary layer and x the amount of salt dissolved in time t. When, however, the process is diffusion controlled the rate, $\frac{dx}{dt}$, is given by

$$\frac{dx}{dt} = \left(\frac{D}{\delta}\right).A(C_y - C_x) \quad \ldots\ldots\ldots\ldots (12)$$

where C_x is the concentration in the bulk of the solution, δ the apparent thickness of the phase boundary layer and D the diffusion coefficient.[81] In the general case it follows that

$$\frac{dx}{dt} = \left(\frac{aD}{D + a\delta}\right).A(C_s - C_x) \ldots\ldots\ldots\ldots(13)$$

so that the rate constant k used by Ezrokhi[79] and defined by:

$$\frac{dx}{dt} = kA(C_s - C_x) \ldots\ldots\ldots\ldots(14)$$

is also given by:

$$\frac{1}{k} = \frac{1}{a} + \frac{\delta}{D} \ldots\ldots\ldots\ldots(15)$$

Since δ and D both depend on the viscosity, η, of the phase-boundary solution,[81,82] equation (15) may be written as:

$$\frac{1}{k} = \frac{1}{a} + f(\eta) \ldots\ldots\ldots\ldots(16)$$

From this equation Zdanovskii[81] distinguishes three kinetic types of behaviour.

(i) pure diffusion, when $\eta \rightarrow 0$, $\frac{1}{k} \rightarrow 0$ and $a \rightarrow \infty$;

(ii) an intermediate type, when $\eta \rightarrow 0$, $\frac{1}{k} \rightarrow \frac{1}{a}$; and

(iii) a pure phase-boundary process, when $k = a$ for all values of η.

At 25°C. the experimental data show that dissolution of sodium chloride in water containing increasing concentrations of calcium chloride, of magnesium chloride or of a mixture of sodium chloride, potassium chloride and magnesium chloride is of the first kinetic type.[81]

All the original papers on this subject to which reference has already been made give numerical data on rock salt dissolution in aqueous solution.

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Molar and Molal Volumes

For normal and blue crystals of rock salt the molar volume is 27·0 c.c.[1] The apparent molar volumes of aqueous solutions of sodium chloride at 0°C. are linear functions of the square root of the volume concentration between 0·2 and 0·5 N., but for concentrations less than 0·2 N. the graph shows a distinct curvature,[2] with a slightly sigmoid character between 0·01 and 1·0 N. at 25°C.[3] At 0°C. the apparent molar volume at infinite dilution, ϕ_0 (NaCl), is $12{\cdot}70_4 \pm 0{\cdot}003$ c.c. Data on the apparent molar volumes of aqueous sodium chloride at several temperatures (0·06°, 25°, 45°, 65° and 85°C.) are available in tabular and graphical form.

The apparent molal volume, ϕ, in c.c., of a sodium chloride solution the density of which is d g. c.c.$^{-1}$ is given at 35°C., by:[5]

$$\phi = 18{\cdot}10 + 1{\cdot}24\sqrt{d}$$

Whereas the value for the apparent molar volume of sodium chloride in liquid ammonia is considerably smaller than that in water at the same temperature and concentration (in mole fraction), the increase in apparent molar volume with increasing concentration is much bigger for the ammonia solutions.[6]

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Electrolytic Conductance, Transference Numbers and Electrochemical Properties of Sodium Chloride Solutions

Conductance.

Aqueous Solutions.

From the accepted values[1] of the ionic conductances at infinite dilution, (λ_1^0 for the cation, λ_2^0 for the anion), the equivalent conductance at infinite dilution, Λ^0, of sodium chloride at 25°C. is, by Kohlrausch's principle

$$\Lambda^0 = \lambda_1^0 + \lambda_2^0 = 50{\cdot}11 + 76{\cdot}34 = 126{\cdot}45\,\text{ohm}^{-1}\,\text{cm.}^2$$

At 15°, 35° and 45°C., the equivalent conductances, Λ^0, have been very accurately determined to be 101·18, 153·75 and 182·65 ohm cm.^{2} respectively.[2]

The variation of conductance with concentration is given in Table XLIV.

TABLE XLIV.- EQUIVALENT CONDUCTANCE OF SODIUM CHLORIDE IN AQUEOUS SOLUTION AT 25°C.[3 a,b]

Λ (ohm^{-1} cm.^{2})	Concentration (g. equiv. l^{-1})
124·50	0·0005
123·74	0·001
120·65	0·005
118·51	0·01
115·76	0·02
111·06	0·05
106·74	0·1

The conductance of sodium chloride solutions in the range 0·001 to 0·000067 N. at 25°C.,[4] as well as the conductance of 0·0001 to 0·000004 N. solutions in the temperature ranges 15° to 25°C.[5] and 5° to 65°C.[6-8] has been determined. The temperature coefficient of the conductance in the former range is 0·0225 ohm^{-1} cm.^{2} deg.$^{-1}$.[5] Copeland *et al.*,[9] from their measurements of equivalent conductance at 378°, 383°, 388° and 393°C. at different steam densities, have deduced that the salt behaves as a weak electrolyte at all steam densities, the equilibrium constant, K, for the ion-pair formation decreasing from about 9×10^{-3} to 6×10^{-7} as the steam density decreases from 0·4 to 0·2 g. c.c.$^{-1}$ These results may, however, be equivocal, as it has since been demonstrated[10] that dilute solutions of sodium chloride in water between 375° and 400°C. exhibit two phases, a liquid-like phase having a conductance that is relatively unaffected by changes in steam pressure, and another phase, above this, the conductance of which is greatly affected by changes in steam pressure and density. It seems probable that Copeland measured the average conductance of these two phases.[10] The conductance of dilute and concentrated solutions has been investigated under pressures of up to 4000 atm. and at 0°, 25° and 30°C.[11] It was found that an increase in pressure enhances the conductance of concentrated solutions and depresses that of dilute solutions. Moreover, at high pressures, the conductance as a function of concentration reaches a maximum at concentrations close to saturation and then decreases.[11]

The conductance of any electrolyte solution is increased by applying an alternating potential the frequency of which is high enough for the time of oscillation to be small in comparison with the relaxation time of the ionic atmosphere. This (Debye–Falkenhagen) effect has been studied using sodium chloride on a number of occasions.[12-16] The conductance at low frequencies[17] and in the region of decimeter waves[18] has also been studied. In his pioneer work on the influence of high voltages on the conductance of solutions, Wein[19] measured the magnitude of the increase for sodium chloride solutions.

Data are available for the conductance of sodium chloride in deuterium oxide solutions at concentrations of approx. 0·16 g. equiv. l.$^{-1}$,[20] and in water containing 0–94% deuterium oxide at concentrations of 0·02 N.[21] The equivalent conductance at infinite dilution in pure deuterium oxide is smaller[20] (104·50 ohm^{-1} cm.^{2}), but the temperature coefficient of conductance from 25° to 45°C. is greater[21] than the corresponding values in ordinary water.

Of the various theoretical treatments of electrolyte solutions prior to 1952, that due to Debye, Hückel and Onsager was one of the few that could accommodate, with any measure of success, the known experimental values of the electrolytic conductance. Even so, this theory accounted only for the data for uni-univalent electrolytes up to 0·001 N., the equation for aqueous solutions at 25°C. being

$$\Lambda = \Lambda^0 - (0{\cdot}2289\,\Lambda^0 + 60{\cdot}32)\sqrt{c} \;\ldots\ldots\ldots\ldots(1)$$

where c is the molarity.

Falkenhagen *et al.*[22] in 1952, and Fuoss and Onsager[23] in 1955, by making allowance for the finite size of an ion, extended the range of application of solution theory to higher concentrations. The Falkenhagen equation for sodium chloride solutions may be written:

$$\Lambda = \Lambda^0 - (B_1\Lambda^0 + B_2).\,\frac{\sqrt{c}}{1 + Ba\sqrt{c}} \;\ldots\ldots\ldots\ldots(2)$$

where B_1, B_2 and B are constants (determined by the temperature, dielectric constant and viscosity of the solvent) the values of which for aqueous solutions at various temperatures have been tabulated,[24] and a is the distance of closest approach of the ions expressed in Angstrom units (A).

Stokes and Robinson[25] have shown that this equation, with a = 4·0, represents the conductance of sodium chloride solutions at temperatures from 15° to 45°C. within the experimental error up to 0·1 N. (Table XLV). The significant feature of equation (2) is that the parameter a is the same for all temperatures in the stated range, which implies that it is a real molecular dimension and not simply an arbitrary constant.

TABLE XLV.- THE CONDUCTANCE OF SODIUM CHLORIDE SOLUTIONS AT 25°C.[24]

Concentration (moles l.$^{-1}$)	Λ obs.	Λ (Eqn. 2)*	Λ (Eqn. 1)
0·0005	124·51	124·51	124·45
0·001	123·74	123·75	123·63
0·002	122·66	122·68	122·46
0·005	120·64	120·68	120·14
0·01	118·53	118·57	117·53
0·02	115·76	115·81	113·83
0·05	111·06	111·03	106·50
0·1	106·74	106·52	98·23

* B_1 = 0·2289, B_2 = 60·32, B = 0·3286

Conductance of Aqueous Mixtures Containing Sodium Chloride.

Compared with pure sodium chloride solutions, the conductance of which has been studied in detail, mixtures of electrolytes containing sodium chloride have received scant attention. As a result, the theoretical interpretation of the existing experimental data is still awaited, except at extreme dilutions where the Onsager limiting equation applies. Tabulated and graphical data are available for the following binary aqueous mixtures: of sodium chloride with hydrochloric acid,[26-29] potassium chloride,[27,30] lithium chloride,[29] sodium magnesium chloride,[29] and sodium hydroxide.[31]

In methanol and water, (50 mol.-%) the equivalent conductance at infinite dilution, determined by extrapolation of the measurements from 0·01 to 0·0005 N., is 66·62 ohm^{-1} cm.^{2}.[32] This marked decrease of the limiting conductance, compared with that in water, is greater than can be ascribed to the change in viscosity alone.[32] Conductance measurements of sodium chloride in aqueous pyridine[33] and aqueous urea[34] solutions have also been made.

The addition of small amounts of certain non-electrolytes to aqueous sodium chloride solutions influences the conductance appreciably, but the mechanism of this effect is unknown.[35,36] The addition of glycocoll[37] or thiourea[38] is also accompanied by a decrease, but the effect of adding egg albumin[39] depends on the pH of the salt solution. If the albumin is added after the salt solution has been brought to a pH of 3·5 by means of hydrochloric acid, the conductance increases with increasing albumin concentration. At pH values of 5·0 and 7·3 there is, however, a decrease with increasing concentration of albumin. The specific conductance at various dilutions of sodium chloride is less in aqueous solution than the specific conductance in a 2% agar sol, which in turn, is less than that in a 2% agar gel.[40]

Transference Numbers.

Tables XLVI and XLVII give the variation of transference numbers of the sodium ion in aqueous sodium chloride solution with concentration and temperature respectively.

TABLE XLVI.- TRANSFERENCE NUMBER OF SODIUM ION IN AQUEOUS SODIUM CHLORIDE AT 25°C.[41,41a]

C (moles l.$^{-1}$)	t_1 (observed)	t_1 (calculated)
0·0	0·3962	0·3962
0·01	0·3918	0·3918
0·02	0·3902	0·3902
0·05	0·3876	0·3875
0·10	0·3854	0·3849
0·20	0·3821	0·3819

TABLE XLVII.- INFLUENCE OF TEMPERATURE ON SODIUM ION TRANSFERENCE NUMBER IN 0·01 M. SODIUM CHLORIDE[1]

t_1	t°C.
0·387	0
0·397	18
0·404	30

The transference number of the sodium ion decreases with increasing concentration according to the predictions of the extended Debye-Hückel theory: for uni-univalent electrolytes the cation transference number is given by:[24]

$$t_1 = \frac{\lambda_1^0 - \frac{1}{2}B_2\sqrt{c}/(1 + \kappa a)}{\Lambda^0 - B_2\sqrt{c}/(1 + \kappa a)} \quad \text{..........(3)}$$

where $B_2 = 82{\cdot}5/\eta(\epsilon T)^{1/2}$, $\kappa a = B a\sqrt{I}$ and I is the ionic strength. Values of the dielectric constant, ϵ, and viscosity, η, together with values of B and B_2 have been tabulated.[24] At 25°C., $B_2 = 60{\cdot}32$ and $B \times 10^{-8} = 0{\cdot}3286$.

From equation (3) it can be seen that, as λ_1^0/Λ^0 is less than 0·5, t_1 will decrease with increasing concentration. Column three of Table XLVI gives the calculated values of the transference number, the parameter a in equation (3) being taken as $5{\cdot}2 \times 10^{-8}$.

Transference numbers of ions in aqueous alkali halide mixtures and in hydrochloric acid-alkali halide mixtures have been determined.[42-44] Very recently, the transference numbers in electrolytes under pressure have been investigated: more than a 2% decrease in cation transference number was observed for 0·1 M. sodium chloride solutions under a pressure of approximately 1000 atm.[45]

Conductance and Transference Numbers of Sodium Chloride in Non-Aqueous Media.

The measurements of Gordon[24,46,49] *et al.* on the conductance of electrolytes and transference numbers of ions in anhydrous methanol constitute the most precise information on the transport properties of ions in non-aqueous media so far obtained. Their results for sodium chloride are summarized in Tables XLVIII, XLIX and L.

TABLE XLVIII.- TRANSFERENCE NUMBER OF SODIUM ION IN METHANOL AT 25°C.[46]

C moles $l.^{-1}$	t_1
0	0·4633
0·003	0·4603
0·005	0·4595
0·007	0·4588
0·01	0·4582

TABLE XLIX.- LIMITING IONIC CONDUCTANCE IN METHANOL AT 25°C.[47]

Ion	Na^+	Cl^-
λ^0 ohm^{-1} $cm.^2$	45·22	52·38

TABLE L.- EQUIVALENT CONDUCTANCE OF SODIUM CHLORIDE IN METHANOL AT 25°C.[47,47a]

$C \times 10^4$ moles $l.^{-1}$	Λ ohm^{-1} $cm.^2$
0	97·61
2	94·11
5	92·09
10	89·87
20	86·91
30	84·84
50	81·80
70	79·43
100	76·71

Gordon[47] *et al.* found that in the empirical equation:

$$\Lambda = \Lambda^0 + \alpha c + \beta c \log c \qquad \text{..........(4)}$$

the coefficients Λ^0, α and β are respectively 97·61, 1120 and 375 at 25°C. In this equation c is the molar concentration. From their data, and with the value of a taken as 5·9 (A.), equation (3) becomes

$$t_1 = \frac{45{\cdot}22 - 78{\cdot}1\sqrt{c}/(1 + 3{\cdot}06\sqrt{c})}{97{\cdot}61 - 156{\cdot}2\sqrt{c}/(1 + 3{\cdot}06\sqrt{c})} \qquad \text{..........(5)}$$

Equation (5) reproduces the observed transference number data up to 0·01 M. (Table L) within 0·0001.[24]

Very little quantitative data has been published on the transport phenomena of sodium chloride in other non-aqueous solutions. It is known that the dependence of equivalent conductance on concentration in ethanol solutions differs from the dependence in methanol.[48] In liquid ammonia conductance measurements have been made at +15° and –40°C.[49,50] and the Debye-Hückel-Onsager theory is applicable at concentrations below 4×10^{-6} M. at –40°C.[50] The equivalent conductances at higher concentrations at 15°C. are as shown in Table LI.

TABLE LI.- CONDUCTANCE OF SODIUM CHLORIDE IN LIQUID AMMONIA AT 15°C.[49]

Λ (ohm^{-1} cm.^{2})	c (moles l.$^{-1}$)
100	0·04$_5$
150	0·01
220	0·003$_3$
300	0·001
500	0·0001
570	0·00003

In fused acetamide at 90°C. the equivalent conductance-concentration curve for sodium chloride is similar to that in water.[51] The conductance at various concentrations of sodium chloride in selenium oxychloride at 25°C. has been determined.[52]

Electrolysis of Sodium Chloride Solutions.

This is a subject of immense practical importance. It is the basis of the large-scale manufacture of chlorine and caustic soda and the preparation, on a smaller scale, of the perchlorate, chlorate and hypochlorites of sodium. Elsewhere in this Supplement, in the sections dealing with these substances, the industrial aspects of the electrolyses have already been treated. Smith[53] has discussed the following: the operating data, including current densities, cell voltages, cell temperatures, potential drops through cells, energy efficiency, electrode consumption rate and the sodium chloride contents in the inlet and outlet electrolytes, of the various types of diaphragm and mercury cells; reactions in the catholyte; the discharge of chloride and hydroxyl ions at platinum, Acheson graphite and magnetite anodes; and the hydrogen discharge potential at a mercury cathode and the influence on this of cations in the feed brine.

Several original papers have dealt with the more fundamental considerations of decomposition voltages[54] of sodium chloride solutions and discharge potentials of the sodium ion,[55-61] the hydrogen ion[55,62-66] and the chloride ion[55,67] under more stringently defined conditions.

The results of investigations into the electrolysis of 3% and 10% solutions of sodium chloride in liquid ammonia are available in graphical and tabular form;[68,69] the decomposition voltage is approx. 3·54 V. at room temperature, and sodamide and ammonium chloride are formed at the cathode and anode respectively.

Electrokinetic and Miscellaneous Electrochemical Properties of Sodium Chloride Solutions.

The zeta-potentials at a cellulose interface of aqueous sodium chloride solutions over a concentration range up to approximately 0·001 N. and aqueous mixtures of sodium and potassium chlorides have been measured at temperatures between 20° and 51°C.[70-72] For 1×10^{-4} N. sodium chloride the potential has a slight maximum in the neighbourhood of 40°C.[71] The streaming potential,[73,74] E, produced by the flow of a dilute sodium chloride solution through fine-pore quartz membranes is directly proportional to the driving pressure, P, up to 300 g. cm.$^{-2}$, and the ratio E/P is the smaller the greater is the concentration of the solution and the smaller the particle diameter, D. Table LII summarizes published data.[73]

TABLE LII.- STREAMING POTENTIALS OF SODIUM CHLORIDE SOLUTIONS

D (microns)	*E/P* (V. cm.^{2} g.$^{-1}$)	
	1 × 10^{-5} N.	5 × 10^{-2} N.
115	11	0·058
39	10	0·061
10–1	2·1	0·032
1	0·5	0·030

On the basis of experimental evidence for the extent of hydration of sodium chloride in 0·005 N. solutions, Darmois[75] has interpreted electro-osmosis, hitherto attributed to the existence of a Helmholtz double layer, in terms of the transport of water by ions. He has derived an equation, applicable to sodium chloride solutions, that relates the rise of one solution and the fall of another when they are separated by a porous diaphragm and connected via metal electrodes to a source of electromotive force, to the viscosity, to the mobilities of the ions and to the number of water molecules of hydration.

The theory of the distribution potential resulting from the partitioning of one or more salts between two solvents has recently been tested using the chlorides of sodium and potassium.[76,77] If $\Delta\psi$ and $\Delta\nu$ are the outer and surface potentials respectively, then the distribution potential, $\Delta\phi(= \Delta\psi + \Delta\nu)$, when $\Delta\nu \rightarrow 0$ is given by

$$\Delta\phi = \frac{\boldsymbol{R}T}{2F} \ln\frac{B\mathrm{Na}^+}{B\mathrm{K}^+} \ldots\ldots\ldots\ldots(6)$$

where B is the ionic distribution coefficient and $\boldsymbol{R}$, T and F have their usual meaning. Equation (6) is valid when appreciable solubility of the salt exists in both solvents as would be the case for sodium chloride distributed between water and a polar oil. When there is little solubility in one solvent, for instance, when the solvents are water and a non-polar oil, then $\Delta\psi \rightarrow 0$ and

$$\Delta\phi = \frac{\boldsymbol{R}T}{2F} \ln\frac{S_{\mathrm{Na}^+}}{S_{\mathrm{K}^+}} \ldots\ldots\ldots\ldots(7)$$

where S is the ratio of the concentration of the salt in one solvent to that in the other.[76]

It has been shown[78] that the action of a shale barrier separating two sodium chloride solutions of different concentrations is analogous to that of a glass membrane separating two acid solutions of different hydrogen ion concentrations. The shale behaves as a 'sodium' electrode and is responsive to the activities of the sodium ions in the two solutions in such a way that the potential can be calculated by means of the Nernst equation.

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Activity and Activity Coefficients of Sodium Chloride

The chemical potentials of the components of aqueous sodium chloride solutions have probably been determined more often than those of any other electrolyte solution. Reliable and extremely consistent results have been obtained by several investigators using chiefly the vapour pressure, depression of freezing point and electromotive force methods. Consequently, sodium chloride solutions are now used as standards in the isopiestic vapour pressure method of determining the activity and osmotic coefficients of other electrolyte solutions. It is instructive to illustrate the agreement that can be reached by different workers. Brown and MacInnes[1] determined the activity coefficient of sodium chloride (0·1 M.) from the potential of a concentration cell with transference and found $-\log\gamma_{\mathrm{NaCl}}$ to be 0·1088, where γ_{NaCl} is the mean ionic activity coefficient of sodium chloride on the molality scale. Harned and Cook,[2] who recorded the e.m.f. of cells without transference, arrived at a value for $-\log\gamma_{\mathrm{NaCl}}$ of 0·1085 at the same concentration, while Janz and Gordon,[3] who repeated the cell measurements of Brown and MacInnes,[1] found exactly 0·1088.

Table LIII gives the activity coefficients, the osmotic coefficients and the water activities of aqueous sodium chloride solutions. The osmotic coefficient, ϕ, is, by definition, equal to $-(55{\cdot}51/\nu m)\ln a_w$ for aqueous solutions, ν being the number of ions per mole of electrolyte, m the molality and a_w the water activity, which, in turn, is equal to the ratio of the vapour pressure of the solution to that of pure water.

Table LIV contains similar data for more dilute solutions.

The Debye-Hückel equation

$$\log f = \frac{-A|z_1z_2|\sqrt{I}}{1 + Ba\sqrt{I}} \quad \ldots\ldots\ldots(1)$$

TABLE LIII.- THE ACTIVITY COEFFICIENTS, OSMOTIC COEFFICIENTS AND WATER ACTIVITIES OF SODIUM CHLORIDE SOLUTIONS AT 25°C.[4,5]

Molality m	γ	ϕ	a_w
0·1	0·7784	0·9324	0·996646
0·2	0·7347	0·9245	0·993360
0·3	0·7098	0·9215	0·99009
0·4	0·6928	0·9203	0·98682
0·5	0·6812	0·9209	0·98355
0·6	0·6726	0·9230	0·98025
0·7	0·6668	0·9257	0·97692
0·8	0·6623	0·9288	0·97359
0·9	0·6592	0·9320	0·97023
1·0	0·6569	0·9355	0·96686
1·2	0·6543	0·9428	0·9601
1·4	0·6545	0·9513	0·9532
1·6	0·6573	0·9616	0·9461
1·8	0·6619	0·9723	0·9389
2·0	0·6676	0·9833	0·9316
2·2	0·6746	0·9948	0·9242
2·4	0·6830	1·0068	0·9166
2·6	0·6922	1·0192	0·9089
2·8	0·7025	1·0321	0·9011
3·0	0·7137	1·0453	0·8932
3·2	0·7259	1·0587	0·8851
3·4	0·7385	1·0725	0·8769
3·6	0·7527	1·0867	0·8686
3·8	0·7677	1·1013	0·8600
4·0	0·7832	1·1158	0·8515
4·2	0·7998	1·1306	0·8428
4·4	0·8170	1·1456	0·8339
4·6	0·8352	1·1608	0·8250
4·8	0·8540	1·1761	0·8160
5·0	0·8740	1·1916	0·8069
5·2	0·8949	1·2072	0·7976
5·4	0·9162	1·2229	0·7883
5·6	0·9389	1·2389	0·7788
5·8	0·9622	1·2548	0·7693
6·0	0·9862	1·2706	0·7598

The vapour pressures in column 4 are tabulated relative to p^0 = 23·756 mm. for pure water at 25°C.

TABLE LIV.- OSMOTIC COEFFICIENTS OF SODIUM CHLORIDE SOLUTIONS AT 25°C.[6]

m	ϕ	m	ϕ
0·031630	0·9514	0·07142	0·9378
0·03571$_5$	0·9494	0·07279	0·9375
0·03717$_0$	0·9487	0·08703	0·9346
0·04573$_3$	0·9452	0·08942	0·9342
0·05028	0·9437	0·09690	0·9328
0·06051	0·9406	0·09916	0·9325
0·06764	0·9387	0·09983	0·9324

in which f is the mean rational activity coefficient of an electrolyte dissociating into ν_1 cations of valency z_1 and ν_2 anions of valency z_2, I the ionic strength,

A and B constants and a, an adjustable parameter (the distance of closest approach of the ions), is capable of representing the observed activity coefficients with good accuracy by choosing a physically reasonable value of the parameter a. For instance, if a is taken as 3·04 A., equation (1) becomes, at 25°C.,

$$\log f = \frac{-A|z_1z_2|\sqrt{I}}{1+\sqrt{I}}\text{..........(2)}$$

This is the Güntelburg equation,[7] and it gives a fair representation of the behaviour of a number of electrolytes, including sodium chloride, up to I = 0·1. If, however, an additional term containing an adjustable parameter b is included:[8]

$$\log f = -\frac{A|z_1z_2|\sqrt{I}}{1+\sqrt{I}} + b\sqrt{I}\text{..........(3)}$$

the Güntelburg equation is greatly improved. And, with b = 0·150, equation (3) gives values of f for sodium chloride solutions which are in almost perfect agreement with those observed up to m = 0·1.

In default of a rigorous theory of ionic solution covering more realistic concentrations, probably the most successful equation is that derived by Stokes and Robinson.[4,9]

$$\log \gamma = -\frac{A|z_1z_2|\sqrt{I}}{1+Ba\sqrt{I}} - \frac{n}{\nu}\log a_A - \log\{1 + 0{\cdot}001\, W_A\,(\nu - n)m\}\text{..........(4)}$$

where n, the solvation number, is the number of moles of solvent that are combined with ν moles of solute ($\nu = \nu_1 + \nu_2$), and a_A and W_A are the solvent activity and solvent molecular weight respectively. This equation fits the experimentally determined activity coefficients of aqueous sodium chloride solutions over a molality range 0·1 to 5·0 with an average difference in γ of 0·002 and a maximum difference of 0·003, if n is taken as 3·5 and a as 3·97 A.[4] The implications and status of the equation (4) have been fully discussed by Stokes and Robinson.[4]

Sodium chloride is one of the few electrolytes on which measurements of activity coefficients have been made over a sufficient temperature range to test the equation

$$\log \gamma = \frac{-A_1}{T} + A_2 - A_3 \log T\text{..........(5)}$$

which can be derived thermodynamically. A_1, A_2 and A_3 are parameters which are characteristic of the electrolyte and its molality; at 1 M., their values for sodium chloride are 535·45, 11·4326 and 3·9679 respectively.[10]

TABLE LV.- ACTIVITY COEFFICIENT OF SODIUM CHLORIDE AT 1 M.[10]

Temp.°C.	γ observed	γ calculated from equation (5)
0	0·638	0·638
15	0·654	0·653
25	0·658	0·658
40	0·655	0·660
60	0·655	0·654
70	0·648	0·648
80	0·641	0·640
90	0·632	0·631
100	0·622	0·621

Harned and Owen[11] have compiled a table of mean activity coefficients of sodium chloride from 0° to 100°C. from the results of several different schools.[12-15] This is reproduced as Table LVI, where *m* is the molal concentration of the salt.

TABLE LVI.- MEAN ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE[11]

m	0·1	0·2	0·5	1·0	1·5	2·0	2·5	3·0	3·5	4·0
0°C.	0·781	0·731	0·671	0·638	0·626	0·630	0·641	0·660	0·687	0·717
5°C.	0·781	0·733	0·675	0·645	0·636	0·643	0·659	0·677	0·706	0·740
10°C.	0·781	0·734	0·677	0·649	0·643	0·652	0·667	0·691	0·721	0·757
15°C.	0·780	0·734	0·678	0·652	0·648	0·659	0·677	0·702	0·735	0·772
20°C.	0·779	0·733	0·679	0·654	0·652	0·665	0·684	0·712	0·744	0·783
25°C.	0·778	0·732	0·678	0·654	0·658	0·670	-	0·718	-	-
30°C.	0·777	0·731	0·679	0·659	0·658	0·674	0·695	0·724	0·756	0·797
35°C.	0·776	0·730	0·679	0·657	0·660	0·676	0·697	0·726	0·759	0·800
40°C.	0·774	0·728	0·678	0·657	0·661	0·678	0·698	0·728	0·761	0·802
50°C.	0·770	0·725	0·675	0·656	0·662	0·678	0·699	0·728	0·762	0·802
60°C.	0·766	0·721	0·671	0·654	0·659	0·676	0·696	0·726	0·760	0·799
70°C.	0·762	0·717	0·667	0·648	0·655	0·672	0·692	0·721	0·758	0·791
80°C.	0·757	0·711	0·660	0·641	0·646	0·663	0·685	0·712	0·742	0·777
90°C.	0·752	0·705	0·653	0·632	0·638	0·651	0·674	0·700	0·730	0·763
100°C.	0·746	0·698	0·644	0·622	0·629	0·641	0·659	0·687	0·716	0·746

Activities in Aqueous Electrolyte Mixtures Containing Sodium Chloride.

Besides being of importance in industrial and physiological processes, the activities of the components of mixed electrolytes are of considerable theoretical interest. Excellent accounts of the subject, in which aqueous mixtures containing sodium chloride figure prominently, have been given in books by Harned and Owen[11] (Chapter 14) and by Stokes and Robinson[4] (Chapter 15).

In this field most attention has been devoted to sodium chloride–hydrochloric acid mixtures,[4,11,16] closely followed by mixtures of sodium chloride and potassium chloride,[4,11,17-19] sodium chloride and caesium chloride,[4,11,20] and sodium chloride and lithium chloride.[4,11] Considering the sodium chloride–hydrochloric acid system, starting first with solutions containing only hydrochloric acid, it is found that, as the proportion of sodium chloride is increased, the activity coefficient of hydrochloric acid decreases. On the other hand, starting with solutions containing only sodium chloride and then increasing the proportion of hydrochloric acid in the mixture, the activity coefficient of sodium chloride increases. By extrapolation, it becomes possible to determine the activity coefficient of hydrochloric acid in the limiting case of zero hydrochloric acid concentration in a solution in which the electrolyte is virtually all sodium chloride. Likewise, the activity coefficient of sodium chloride in a solution in which the electrolyte is virtually all hydrochloric acid can also be determined. In practice these two limiting values turn out to be nearly identical,[4] as can be seen from Table LVII. $\gamma_{HCl(o)}$ and $\gamma_{NaCl(o)}$ denote the activity coefficients of hydrochloric acid and sodium chloride in solutions containing only hydrochloric acid and sodium chloride respectively, and $\gamma_{(o)HCl}$ and $\gamma_{(o)NaCl}$, the activity coefficients of hydrochloric acid and sodium chloride in the limiting cases where the electrolyte has been replaced entirely by a second electrolyte, sodium chloride and hydrochloric acid respectively. The properties of the hydrochloric acid–sodium chloride system epitomize the characteristics of most mixed electrolyte solutions, except that $\gamma_{(o)NaCl}$ and $\gamma_{(o)XCl}$ do not approximate quite so closely in other cases.

A useful rule, discovered by Harned,[11] can be applied to mixed electrolyte solutions at constant total molality. This states that the logarithm of the

TABLE LVII.- ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE AND HYDROCHLORIC ACID IN MIXED ELECTROLYTE SOLUTIONS AT 25°C.[4,20a]

Total Molality m	$\gamma_{HCl(o)}$	$\gamma_{(o)HCl}$	$\gamma_{(o)NaCl}$	$\gamma_{NaCl(o)}$
0·5	0·757	0·726	0·727	0·681
1·0	0·809	0·752	0·751	0·657
2·0	1·009	0·875	0·873	0·668
3·0	1·316	1·063	1·066	0·714

activity coefficient of one electrolyte in a mixture at constant total molality is directly proportional to the molality of the other electrolyte. That is

$$\log \gamma_1 = \log \gamma_{1(o)} - \alpha_1 m_2 \quad \ldots\ldots\ldots (6)$$

where the subscripts 1 and 2 refer to the two electrolytes and $\gamma_{1(o)}$ has the significance already mentioned (compare $\gamma_{NaCl(o)}$). From equation (6) it follows that when $m_2 = m$ = total molality

$$\log_{(o)1} = \log_{1(o)} - \alpha_1 m \quad \ldots\ldots\ldots (7)$$

so that

and

$$\left.\begin{aligned} \log \gamma_1 &= \log \gamma_{(o)1} + \alpha_1 m_1 \\ \log \gamma_2 &= \log \gamma_{(o)2} + \alpha_2 m_2 \end{aligned}\right\} \quad \ldots\ldots\ldots (8)$$

In equations (6), (7) and (8), α_1 and α_2 are functions of the individual molalities m_1 and m_2. These equations are obeyed by a large number of mixed electrolyte solutions and are valid over a wide concentration range.[4] A table of values of α_1 and α_2 for sodium chloride-hydrochloric acid and other mixtures has been constructed by Harned and Owen.[11] There is however a notable exception to this rule: the sodium chloride-sodium hydroxide system.[4] In this case, as for the potassium chloride-potassium hydroxide system, it is necessary to use the equations

and

$$\left.\begin{aligned} \log \gamma_1 &= \log \gamma_{1(o)} - \alpha_1 m_2 - \beta_1 m_2^2 \\ \log \gamma_2 &= \log \gamma_{2(o)} - \alpha_2 m_1 - \beta_2 m_1^2 \end{aligned}\right\} \quad \ldots\ldots\ldots (9)$$

As yet no sound method is available for the calculation of the coefficients α (and β) of the above equations from the properties of single electrolyte solutions, except for dilute solution where the Guggenheim-Güntelburg equation (equation (3)) is valid.

Activity Coefficients of Sodium Chloride in Mixed Solvents.

The variation of the activity coefficient of sodium chloride with the dielectric constant of the solvent at different temperatures and molalities has been studied, mainly using methanol-water[21,22] and ethanol-water[23,24] mixtures. The mixed electrolyte system sodium chloride-hydrochloric acid has also been studied in aqueous methanol.[25]

Akerlöf[21] has shown that at 25°C. the logarithm of the activity coefficient of sodium chloride at infinite dilution is approximately inversely proportional to the dielectric constant of the aqueous methanol. It has also been found[25] that for the six solvents containing respectively 10, 20, 30, 40, 50 and 60% by weight of methanol in water, the logarithm of the activity coefficient of sodium chloride varies linearly with the mole fraction of alcohol and is independent of the acid concentration, while the logarithm of the activity coefficient of hydrochloric acid in sodium chloride solutions at 1 M. total ionic strength, and from 0° to 50°C., varies linearly with the molality of the hydrochloric acid.

The activity coefficients of sodium chloride in liquid ammonia at –36·0±0·05°C.,[26] and the activity coefficients of piperidine in aqueous sodium chloride and other salt solutions at 25°C.[27] have also been determined.

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HETEROGENEOUS EQUILIBRIA IN SYSTEMS CONTAINING SODIUM CHLORIDE

By J. P. JONES

Introduction.

For convenience of presentation the systems are divided into seven classes. The first six are classified according to the cations present, and the last group comprises systems containing organic phases. As far as possible, within each class, systems are described in order of increasing complexity, and since many of those described cannot be represented simply, a suitable monograph on phase equilibria should be consulted for description of methods used in representing multicomponent systems.

Systems Containing Sodium Ion.

A study has been made of the system sodium chloride–sodium sulphate by examining the microstructure of the solid in equilibrium with the melt at different temperatures.[1] Etching and polishing of the solid surface, followed by pressing against a celluloid sheet moistened with amyl acetate, serves to produce a celluloid replica of the surface which can then be examined by transmitted light. No solid solution was observed and a simple eutectic

Refs. p. 916

point exists at 34·5 mole-% Na_2Cl_2 and 618°C. Earlier work by Scarpa on the system sodium chloride-sodium hydroxide has been confirmed.[2] As in the system sodium fluoride-sodium hydroxide, solid solutions of two kinds are formed, there being a miscibility gap between them. Thus this system behaves unlike sodium bromide-sodium hydroxide which forms a simple eutectic, and sodium iodide-sodium hydroxide in which compound formation occurs. As a preliminary to the study of more complex systems, the solubility of sodium chloride in water has been determined over the range 10° to 110° C.,[3,4] and the effect of increasing salt concentration on the density and refractive index of solutions has been examined.[5] The solubility of sodium chloride in water increases with increasing temperature; hence for saturated solutions the normal increase in vapour pressure with temperature is opposed by a decrease resulting from higher salt concentrations. This gives rise to a maximum in the vapour pressure versus temperature curve, as shown in Fig. 13, at 401 kg./cm.^{2} and 600°C.[6] The pressure corresponding to 1 atm. cuts the vapour pressure curve at two points *A* and *B* termed the first and second boiling points respectively. *A* is at 108·8°C. and *B* at 780°C.,[9] between these temperatures saturated solution cannot exist. An important consequence of this behaviour is that fusion does not render sodium chloride anhydrous; only on cooling to 780°C. will the system lose all water. The presence of a eutectic at −21·3°C. and a transition $NaCl,2H_2O \rightarrow NaCl$ at 0·15°C. has been reconfirmed.[7] A simple eutectic is formed by the system sodium chloride-sodium pyrophosphate at 725°C. and 78·5% sodium chloride, there being no solid solution.[8] This eutectic is not in agreement with that observed by Le Chatelier (Mellor, II, 683). Vaksberg's investigation of the system sodium chloride-sodium iodide[77] showed a continuous series of solid solutions in good agreement with earlier work. Similar behaviour is exhibited by sodium chloride-sodium bromide, the mixed crystals having a minimum m.p. which has been inferred but not observed.[9] Silver chloride and sodium cyanide both form with sodium chloride a continuous series of mixed crystals possessing neither minimum nor maximum.[9]

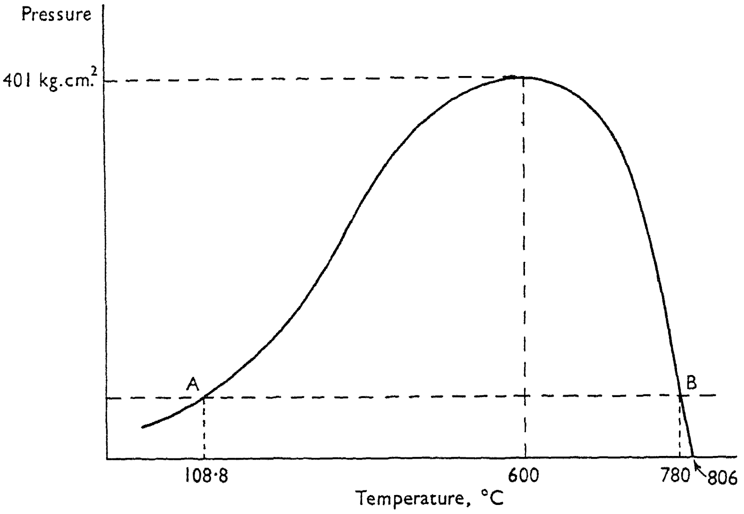


FIG. 13. VAPOUR PRESSURE VERSUS TEMPERATURE CURVE FOR SATURATED SOLUTIONS OF SODIUM CHLORIDE (SCHEMATIC)

Solubility relationships have been determined at 25° and 35° C. in the ternary system sodium chloride-sodium fluoride-water.[10] The compositions, temperatures of transition, and eutectic points, are given in Table LVIII.

TABLE LVIII.- THE SYSTEM SODIUM CHLORIDE-SODIUM FLUORIDE-WATER

Solid Phases	Temp.° C.	Composition of Solution	
		%NaCl	%NaF
Ice + NaF	−3·02	0	4·02
Ice + NaF	−2·98	0	3·82
Ice + $NaCl,2H_2O$	−20·94	23·18	0
Ice + $NaCl,2H_2O$ + NaF	−21·19	23·69	0·24
NaCl + $NaCl,2H_2O$	+0·08	26·39	0
NaCl + $NaCl,2H_2O$	+0·10	26·53	0
NaCl + $NaCl,2H_2O$ + NaF	−0·06	26·25	0·19

Vlasov and Bergman[11,12] have made a careful study of the system sodium chloride-sodium bromide-water. Two fields of solid solution are formed, one of NaCl + $NaBr,2H_2O$, and the other of NaCl + NaBr. This is illustrated in Fig. 14. which represents the isotherm at 25°C. The remaining solid fields are those of ice and $NaBr,5H_2O$. The ternary eutectic at which the fields NaCl + $NaBr,2H_2O$, $NaBr,5H_2O$ and ice meet, is at −29·2°C. and has the composition (moles) NaBr 74·95, NaCl 25·05, H_2O 845. This system has also been studied for the influence of rate of cooling on the composition of the solid phase.[13] Despite formation of sodium chloride-sodium iodide solid solutions at temperatures near the m.p. no solid solutions or double salts have been observed in the system NaCl-NaI-H_2O between 10° and 100° C., the only solid phases present being NaCl, NaI and $NaI,2H_2O$.[14] The ternary system NaCl-NaBr-NaI has been investigated.[15] Mixed crystals are formed in the binary subsystems NaBr-NaI, NaBr-NaCl and a eutectic is formed by NaCl-NaI. In the ternary system ternary solid solution gives rise to a single crystallization plane which splits near the binary NaCl-NaI to give two planes of limited solid solution. Freeth[16] has examined the solubility of sodium chloride plus sodium hydroxide in water at nine temperatures between 0° and 60°C. and shown the system to be of the simplest type involving only the anhydrous components as solids. Antropoff[17] has examined the system from the eutectic point to 800° C. Chrétien[18-20] has made a careful study of the system NaCl-$NaNO_3$-H_2O by determining the solubility of one salt in the presence of various quantities of the other; Holzl and Crotogino[21] examined the system between 0° and 103°C., Khitrova[7] from 0° to 25°C., while others have examined this system as

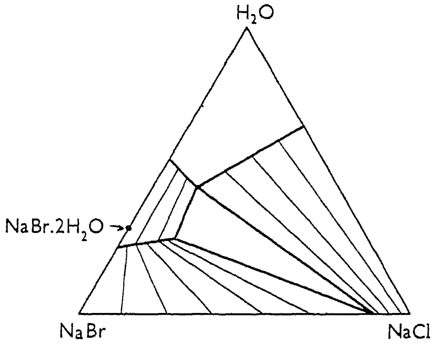


FIG. 14. 25° ISOTHERM FOR THE SYSTEM NaCl-NaBr-H_2O

part of more complex systems.[22,23] A eutectic is formed at −24·3,[20] −24·5,[7] −25·9.[21] The solids NaCl,$2H_2O$, NaCl, NaOH coexist at −5·8°C.,[7] −5·85°C.[20] above which sodium chloride is anhydrous. A solution saturated with respect to both salts boils at 121·4° C.[20] and at 119° C. under 735 mm. pressure.[21] Foote and Schairer[10] examined the system NaCl-Na_2SO_4-H_2O: Table LIX gives the temperatures and compositions of the transitions and eutectics they observed.

TABLE LIX.- THE SYSTEM SODIUM CHLORIDE-SODIUM SULPHATE-WATER

Solid Phase	Temp.°C.	Composition of Solution	
		%Na_2SO_4	%NaCl
Ice + NaCl,$2H_2O$	−20·94	0	23·18
Ice + Na_2SO_4,$10H_2O$	−1·11	3·97	0
Ice + Na_2SO_4,$10H_2O$	−1·14	4·11	0
Ice + Na_2SO_4,$10H_2O$ + NaCl,$2H_2O$	−21·32	0·31	23·43
Na_2SO_4 + Na_2SO_4,$10H_2O$	32·383	33·24	0
Na_2SO_4 + Na_2SO_4,$10H_2O$ + NaCl	17·90	7·77	22·31
NaCl,$2H_2O$ + NaCl	0·08	0	26·39
NaCl,$2H_2O$ + NaCl	0·10	0	26·53
NaCl,$2H_2O$ + NaCl + Na_2SO_4,$10H_2O$	0	1·32	25·79

This system was also studied by Chrétien[20] from 109·1°C., (b.p. of solution saturated with respect to both salts) to the eutectic point −21·7°C. Knowledge of this phase diagram has been applied to the study of conditions necessary for simultaneous separation of sodium chloride and sodium sulphate decahydrate from the brine of Kara Bogatz Bay.[24] Other workers[25-28] have studied the system, usually as part of more complex systems. An unusual experimental approach to the analysis of phase systems has been made by Usanovich and Mun.[5] By determining the density *d* and refractive index *n* of aqueous solutions of sodium chloride, of sodium sulphate and of known ternary mixtures it is possible to analyse rapidly any given ternary system. The method has been exemplified by, but need not be restricted to, the system discussed. Ravich and Borovaya[6,29] studied the system at elevated pressures. Using an autoclave they observed changes in pressure *p* with water content *x* and with temperature *t*, at pressures up to 350 atm. Breaks in the *p*-*t* and *p*-*x* curves correspond to points at which solid crystallizes out. Thus conditions were observed under which a mixture of salts crystallizes out in the presence of water vapour. On addition of sufficient sodium sulphate, the maximum in the vapour pressure-temperature curve for saturated solutions of sodium chloride is lowered and shifts to a lower temperature, while a maximum corresponding to saturated sodium sulphate solution increases. The magnitude of this effect can be seen from Table LX.

TABLE LX.- EFFECTS OF TEMPERATURE AND PRESSURE ON THE SYSTEM SODIUM CHLORIDE-SODIUM SULPHATE-WATER

%Na_2SO_4	Sodium Sulphate Maximum		Sodium Chloride Maximum	
	Pressure	Temp.°C.	Pressure	Temp.°C.
0	-	-	401	600
20	-	-	350	600
35	160	375	300	590
50	320	430	250	560
70(eutectic)	-	-	225	500

At the eutectic point the vapour pressure curve is stated to be almost coincident with that for pure water. Use of nomograms has been proposed[30] for calculating the composition of samples used in thermal analysis when these are prepared by adding second and third components to initial samples of the first component, and the method has been applied to the study of the system $NaCl-Na_2SO_4-H_2O$. The system sodium thiosulphate-water-sodium chloride has been studied at 25°C.[31] by removing a sample of saturated solution, drying and determining thiosulphate titrimetrically. Solubility data thus obtained show that $Na_2S_2O_3,5H_2O$ is not dehydrated by sodium chloride. Freeth[16] determined solubility relations in the systems $NaCl-NaHCO_3-H_2O$, $NaCl-Na_2CO_3-H_2O$, at 5°C. intervals between 10°C. and 45°C. and at 60°C. The latter system has also been studied over a wider temperature range.[27,32] Three hydrates of sodium carbonate can exist within the range 10°C. to 60°C. and the phase diagram at 30°C. is shown in Fig. 15. The system $NaCl-NaHCO_3-H_2O$ is of the simplest type having two crystallization branches corresponding to the anhydrous components. Isotherms at 0°, 20°, 40°, 60°, 80° and 98°C. have been obtained for the system $NaNO_2-NaCl-H_2O$.[33] The importance of the system $NaNO_3-NaNO_2-NaCl$ in the meat curing industry has led to the study of solid blends obtained by evaporation of aqueous solutions containing these three salts.[34] X-Ray diffraction has shown that provided the total $NaNO_3 + NaNO_2$ content is below 10–12% almost complete inclusion of these in the chloride crystals is obtained. Microscopical examination in polarized light confirms this. Despite considerable differences in lattice characteristics cubic sodium chloride can be grown on the rhombohedral face of sodium nitrate and a solid solution of sodium nitrate and a solid solution of sodium nitrite in sodium chloride facilitates inclusion of sodium nitrate by decreasing this difference in lattice spacing. The usefulness of phase studies in identifying new compounds is illustrated by the examination of the system $NaIO_3-NaCl-H_2O$ using the method of wet residues.[35] This system was studied from the lowest eutectic to 35° and isotherms were obtained at 0°, 15°, 25° and 35°C. The hitherto unknown double salt $2NaIO_3,3NaCl,10H_2O$(*D*) was shown to be stable between −21·2°C. and 24·6°C. The eutectics and transition points are given in Table LXI.

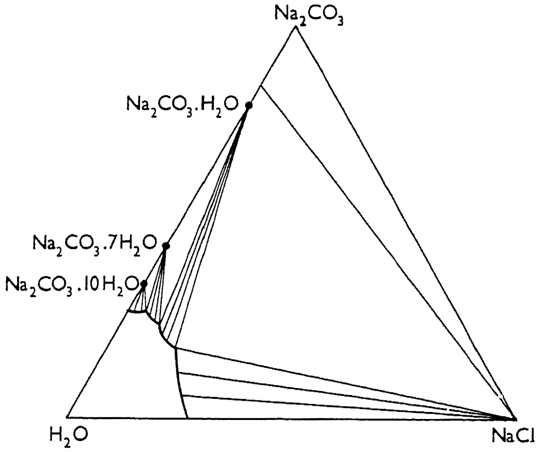


FIG. 15 ISOTHERM AT 30°C. FOR $NaCl-Na_2CO_3-H_2O$ SHOWING THE EXISTENCE OF HYDRATES OF SODIUM CARBONATE

Solubility and density isotherms for the system $Na_2SiF_6-NaCl-H_2O$ at 15°C. show two branches of crystallization intersecting at the point of mutual solubility and have no unusual features.[36] The effect of sodium chloride on the temperature of the transition $Na_2HPO_4,12H_2O \rightarrow Na_2HPO_4,7H_2O$ has been studied.[37] Analysis of the liquid phase at the observed transition temperature enabled compositions at several transition points to be obtained and the resulting phase diagram is shown in Fig. 16.

TABLE LXI.- THE SYSTEM SODIUM CHLORIDE-SODIUM IODATE-WATER

Solid Phases	Temp.°C.	Composition of liquid	
		%$NaIO_3$	%NaCl
Ice, *D*,$NaCl,2H_2O$	−21·18	0·36	23·28
Ice, *D*,$NaIO_3,5H_2O$	−16·9	0·34	19·93
$NaCl,2H_2O \rightarrow NaCl$	0·04		
$NaIO_3,5H_2O \rightarrow NaIO_3,H_2O$	6·8		

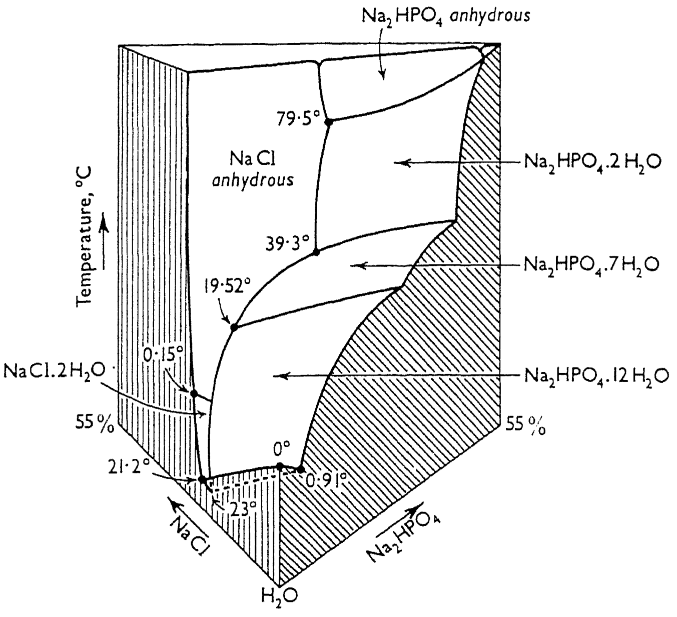


FIG. 16. POLYTHERMAL PHASE DIAGRAM FOR THE SYSTEM Na_2HPO_4-$NaCl$-H_2O

Isotherms for the system $Na_2Cr_2O_7$-$NaCl$-H_2O have been obtained at 0°, 20°, 50° and 75° C.[33] As part of their study of the reciprocal pair NaCl + $Ba(ClO_3)_2$, Capua and Bertoni obtained the 20° isotherm for the system $NaClO_3$-$NaCl$-H_2O.[38] Equilibrium between water, sodium chloride and sodium perchlorate has also been studied at 0°[39] and 100° C. At these temperatures the solid phases are NaCl, $NaClO_4$, $NaClO_4,H_2O$. An unusual feature of the sodium chlorite-sodium chloride-water system is the lack of a break in the solubility curve sodium chlorite trihydrate-sodium chlorite, as is illustrated in Fig. 17. for the isotherm at 25° C.[40]

The system sodium sulphamate-sodium chloride-water forms a simple eutectic at 25° C. and thus resembles the corresponding potassium and ammonium systems.[41] Sodium hydrosulphide-sodium chloride-water constitute a simple system at 20° C., the two solids coexisting with solution of composition 2·06% NaCl, 35·8% NaHS.[42] Visual observation of crystallization points in the fused system $NaCl$-$NaBr$-Na_2SO_4 has revealed two crystallization fields, NaCl + NaBr forming a continuous series of mixed crystals, and Na_2SO_4 crystallizing alone.[43] The system $NaCl$-NaF-Na_2SO_4 is complicated by formation of a compound, Na_2SO_4,NaF;[9] thus four crystallization fields are obtained as shown in the polytherm Fig. 18. Point *S* is a maximum in the eutectic line

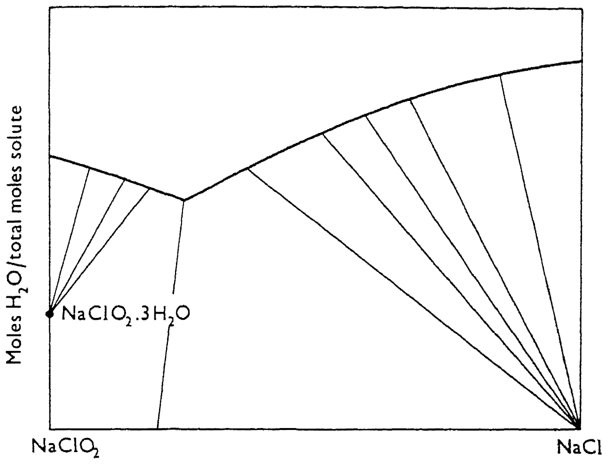


FIG. 17. SOLUBILITY ISOTHERM FOR THE SYSTEM $NaClO_2$-$NaCl$-H_2O AT 25°C. (JANECKE DIAGRAM)

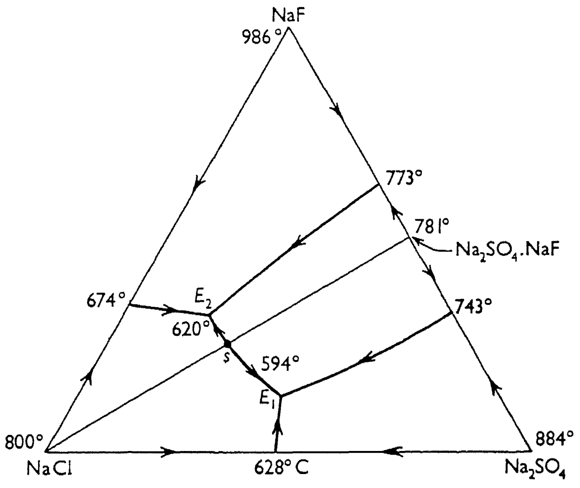


FIG. 18. POLYTHERM OF THE SYSTEM SODIUM CHLORIDE-SODIUM FLUORIDE-WATER, GIVING TEMPERATURE OF EACH INVARIANT POINT

E_1 E_2 and arrows indicate changes in composition of the liquid phase on cooling.

The system sodium sulphite-sodium chloride-water is of the simplest type. Isotherms have been obtained at 0°, 25°, 40°, 60°, 80°, and 100°C. and industrial application of this to the separation of sodium sulphite and sodium chloride is considered feasible.[55] Solubilities of sodium chloride and thiourea in water at 29·93°C. have been obtained by refractive index measurements. A solution saturated with both salt and thiourea has the composition (wt.-%) thiourea 68·7, NaCl 23·5. Sodium chloride decreases the solubility of thiourea appreciably but thiourea has little effect on that of sodium chloride.

Solutions rich in thiourea behave anomalously suggesting the possible existence of two crystalline forms of thiourea.[56]

The commercial importance of Chilean caliche has led to a detailed study of the system $NaNO_3$-$NaCl$-Na_2SO_4-H_2O,[20,44–46,54] the observed eutectics and transition points being given in Table LXII.

TABLE LXII.- THE SYSTEM SODIUM NITRATE-SODIUM CHLORIDE-SODIUM SULPHATE-WATER

Solid Phases	Temp.°C.
$NaNO_3$ $NaNO_3,Na_2SO_4,H_2O$ (darapskite), $NaCl$ $Na_2SO_4,10H_2O$	7·2
$NaNO_3$, $NaCl$, Na_2SO_4	68·5
$Na_2SO_4,10H_2O$, Na_2SO_4, $NaCl$, darapskite	16
$NaCl$, $NaCl,2H_2O$, $NaNO_3$, $Na_2SO_4,10H_2O$	−6
$NaCl,2H_2O$, $NaNO_3$, $Na_2SO_4,10H_2O$, Ice	−24·4
$NaCl,2H_2O \rightarrow NaCl$	0·20
$Na_2SO_4,10H_2O \rightarrow Na_2SO_4$	32·4

Knowledge of the phase relations in this system has been used in considering various possibilities of obtaining saturated solutions from a given caliche.[47] Freeth has determined solubility relations in the systems Na_2CO_3-$NaOH$-$NaCl$-H_2O and Na_2CO_3-$NaHCO_3$-$NaCl$-H_2O at nine temperatures[16] and orthogonal projections of tetrahedra formed using Schreinemakers' method are shown in Figs. 19–26 and 27–34, from which can be seen the influence of temperature on the crystallization fields. Itkina also studied this system at 100°C.[48] obtaining a point of composition NaOH 11·07%, Na_2CO_3 4·93%, NaCl 16·89 at which the transition $Na_2CO_3,H_2O \rightarrow Na_2CO_3$ occurs. At 100°C. the system Na_2CO_3-Na_2SO_4-$NaCl$-H_2O was shown to contain four solid phases: Na_2CO_3, $NaCl$, Na_2SO_4, $m Na_2SO_4, n Na_2CO_3$.[49] This last phase was later shown to be a solid solution containing the compound $2Na_2SO_4,Na_2CO_3$ (burkeite), which is stable above 14·4°C.[27] Itkina studied the system Na_2SO_4-$NaCl$-$NaOH$-H_2O at 25° C as part of a quinary system.[48,50] Of the solids Na_2SO_4, $Na_2SO_4,10H_2O$, $NaCl$, $NaOH$ present at this temperature, Na_2SO_4 takes up the largest crystallization area. The solubility of sodium sulphate is depressed by sodium hydroxide and further reduced by sodium chloride, and dehydration of sodium sulphate occurs at 14·07% NaCl and at 7·73% NaOH. As in the anhydrous ternary system so in the quaternary $NaCl$-Na_2SO_4-NaF-H_2O, the double salt Na_2SO_4, NaF is stable. Solubility isotherms at 25° C. indicate some replacement of NaF in the double salt by an equivalent amount of NaCl.[10]

The effect of pressure on the hydrolysis of sodium carbonate has been studied in the system $NaCl$-Na_2SO_4-(Na_2CO_3 + $NaOH$), the last two components being in constant proportion.[51] A triple salt of formula $4NaOH,4NaCl,5Na_2SO_4$ is reported to be formed when sufficient sodium sulphate is added to certain caustic liquors.[52]

The quinary system Na_2SO_4-Na_2CO_3-$NaCl$-$NaOH$-H_2O has been studied at 100°C.[48] and at 25°.[50] The effect of sodium chloride and sodium hydroxide on the dehydration of hydrates of sodium sulphate and carbonate and on formation of burkeite was studied. At 100°C. two ternary invariant points were obtained at which the solids were Na_2SO_4, $NaCl$ and burkeite, and one point was obtained at which the four solids, Na_2CO_3, Na_2CO_3,H_2O, $NaCl$ and burkeite, coexist. Contrary to the findings of Green and Fratteli Na_2CO_3,H_2O is not stable over the whole range of sodium hydroxide concentrations. Interest in crystallization of trona ($Na_2CO_3,NaHCO_3,2H_2O$) has led to investigation of the system Na_2CO_3-$NaHCO_3$-Na_2SO_4-$NaCl$-H_2O in the region of crystallization of trona and in the temperature range 0 to 65°C. Observations on evaporation of certain brines were then compared with this phase diagram.[53]

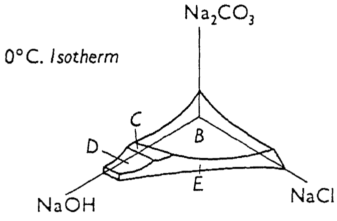

Na_2CO_3
0° C. Isotherm
C
B
D
NaOH
E
NaCl

Fig. 19

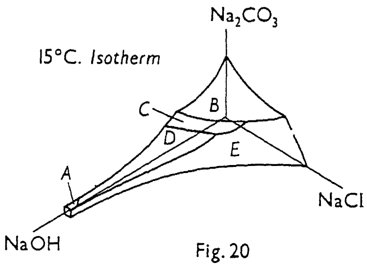

Na_2CO_3
15°C. Isotherm
C
B
D
E
A
NaCl
NaOH

Fig. 20

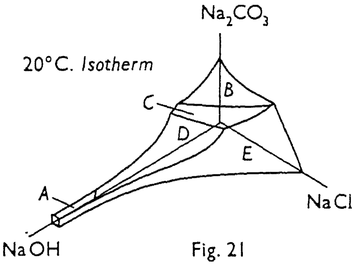

Na_2CO_3
20°C. Isotherm
C
B
D
E
A
NaCl
NaOH

Fig. 21

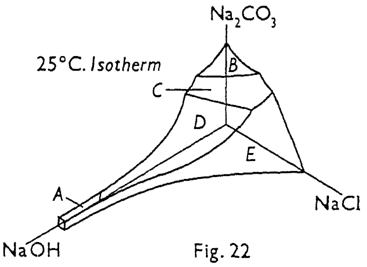

Na_2CO_3
25°C. Isotherm
B
C
D
E
A
NaCl
NaOH

Fig. 22

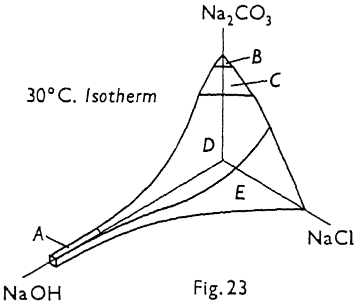

Na_2CO_3
B
C
30°C. Isotherm
D
E
A
NaCl
NaOH

Fig. 23

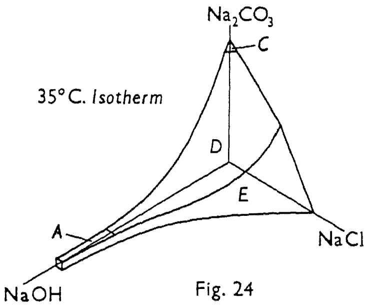

Na_2CO_3
C
35°C. Isotherm
D
E
A
NaCl
NaOH

Fig. 24

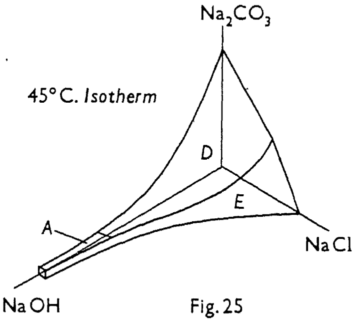

Na_2CO_3
45°C. Isotherm
D
E
A
NaCl
NaOH

Fig. 25

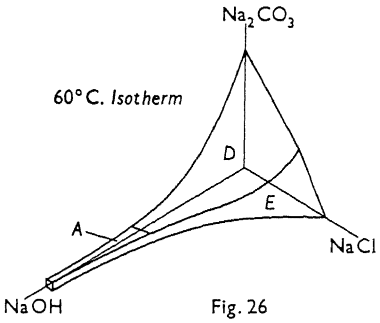
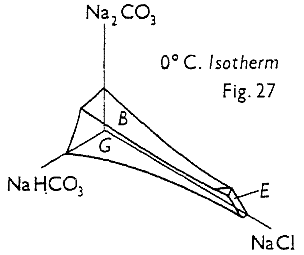
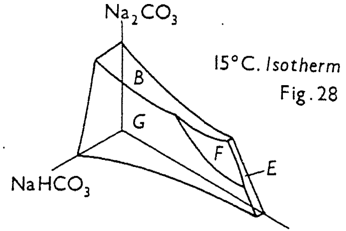
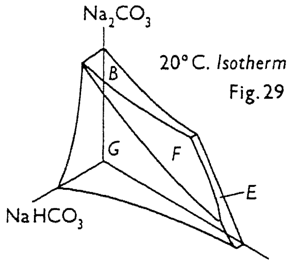

Na_2CO_3
60°C. Isotherm
D
E
A
NaCl
NaOH

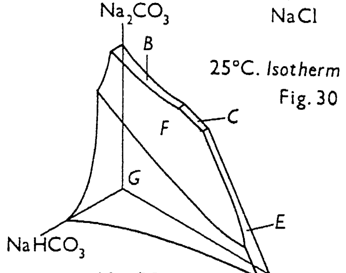
Fig. 26

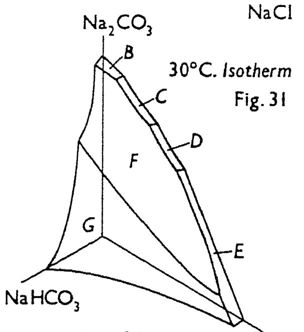
FIGS. 19–26. ISOTHERMS FOR THE SYSTEM $NaOH$-Na_2CO_3-$NaCl$-H_2O (SCHREINEMAKERS' PROJECTION)

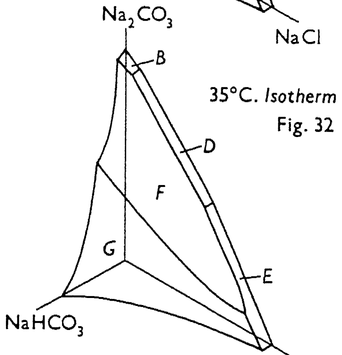

0° C. Isotherm
Fig. 27
Na$_2$CO$_3$
B
G
E
NaHCO$_3$
NaCl

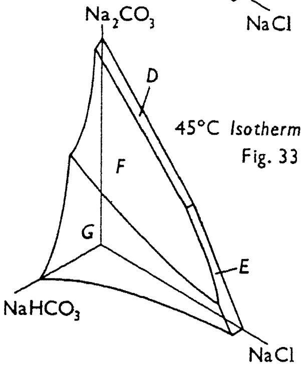

15°C. Isotherm
Fig. 28
Na$_2$CO$_3$
B
G
F
E
NaHCO$_3$
NaCl

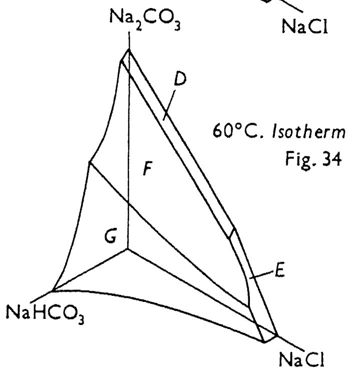

20° C. Isotherm
Fig. 29
Na$_2$CO$_3$
B
G
F
E
NaHCO$_3$
NaCl


25°C. Isotherm
Fig. 30
Na$_2$CO$_3$
B
C
F
G
E
NaHCO$_3$
NaCl


30°C. Isotherm
Fig. 31
Na$_2$CO$_3$
B
C
D
F
G
E
NaHCO$_3$
NaCl


35°C. Isotherm
Fig. 32
Na$_2$CO$_3$
B
D
F
G
E
NaHCO$_3$
NaCl


45°C Isotherm
Fig. 33
Na$_2$CO$_3$
D
F
G
E
NaHCO$_3$
NaCl


60°C. Isotherm
Fig. 34
Na$_2$CO$_3$
D
F
G
E
NaHCO$_3$
NaCl

FIGS. 27–34. ISOTHERMS FOR THE SYSTEM $NaHCO_3$-Na_2CO_3-$NaCl$-H_2O (SCHREINEMAKERS' PROJECTION)

Systems Containing Potassium Ion.

The binary system sodium chloride–potassium chloride forms a continuous series of mixed crystals with a minimum in the m.p. at 664°C.,[9] or at 658°C. and 50% sodium chloride.[58] The homogeneous system persists only over a limited temperature range, partial miscibility commencing at 500°C.[58] or at 490 ± 5°C., and 67 mole-% NaCl.[57] The miscibility gap has been explored by *X*-ray analysis of the solid solutions from the critical solution temperature down to 300°C.[57] and the heat of formation of solid solutions as a function of composition has been found to be well represented by

$$\Delta H = x(1-x)[4350 + 650(1-2x)^2 - 770(1-2x)^3]\text{g.-cal.}$$

where x is the mole fraction of sodium chloride. The aqueous system NaCl–KCl–H_2O has been studied from its ternary eutectic at −23°C. to 200°C.[3,12,59-61] No ternary compound is formed; consequently the features of the constituent binary systems largely determine its behaviour. A polythermal projection of the system is given in Fig. 35. Incongruently melting sodium chloride dehydrate gives rise to a peritectic point *P*. Line *Px* defining the crystallization fields of sodium and potassium chlorides ends at the consolute point *x*, the homogeneous mixed crystal phase forming above this temperature. Point *E* is a-ternary eutectic, ϵ_2 and ϵ_3 being binary eutectics for the systems KCl–H_2O and NaCl,$2H_2O$–H_2O respectively. Based on knowledge of this system a method has been evolved for extracting potassium chloride from sylvite.[62] From pressure–temperature and pressure–water content curves, crystallization points for this system have been obtained at pressures up to 300 atm. and for temperatures between 200° and[29] 600°C. Wood has shown that of 60 possible reactions which may occur between pairs of alkali halides not possessing a common ion, 57 proceed to completion, the stable salt pair being formed by combination of the largest cation and anion. Thus salt pairs NaF–KCl,[64] NaCl–KBr and NaCl–KI are stable. Fig. 36. shows a polythermal square projection of the system obtained by plotting Na/(Na + K) as abscissa and F/(F + Cl) as ordinate.[63] The pair KCl–NaF, being compatible, behaves as a binary system having a minimum at point *M*. Characteristic points of this system

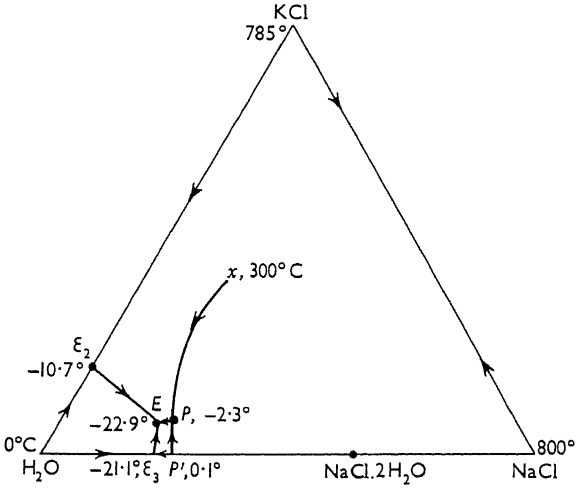


FIG. 35. POLYTHERMAL PROJECTION OF TERNARY SYSTEM KCl–NaCl–H_2O

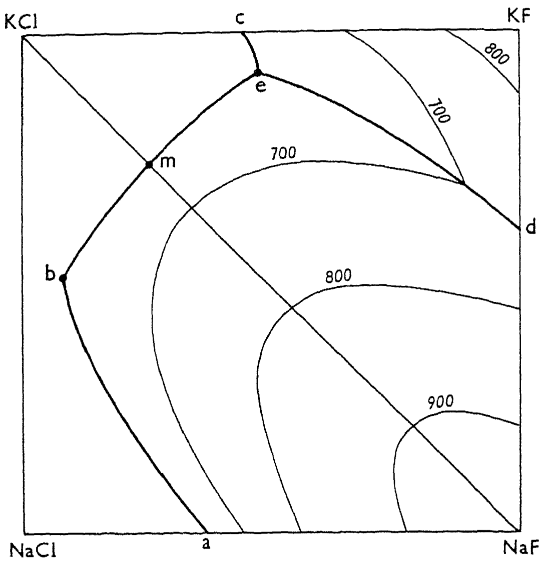


FIG. 36. POLYTHERMAL PROJECTION OF RECIPROCAL TERNARY SYSTEM KCl-NaF (ISOTHERMAL LINES DRAWN AT 100° INTERVALS)

are given in Table LXIII.

TABLE LXIII.- CHARACTERISTIC POINTS OF THE SYSTEM SODIUM CHLORIDE-POTASSIUM FLUORIDE

Point in Fig. 22	Composition (mole-%)	Temp.°C.
a	NaF 33	680
b	K^+ 50, F' 25	612
c	KF 46·1	605
d	NaF 40	722
e	K^+ 90·5 F' 49	582
m	K^+ 72 F' 28	660

Sauerwald and Dombois[65] observed a eutectic at 630°C. and 18% NaF in the system KCl-NaF, one at 680°C. and 28% NaF in the binary system NaCl-NaF and a eutectic at 590°C. and 10% NaF, 35% NaCl (all percentages being by weight). These three eutectics correspond to points *m*, *a* and *b* respectively in Fig. 36. and are thus in good agreement. No breakdown of NaCl-KCl solid solution was observed above the minimum corresponding to point *b* Fig. 36.[64,65] The system NaCl-KI is of interest because mixed crystal formation occurs between sodium iodide and potassium chloride and between sodium chloride and potassium chloride,[77] and so not only are potassium iodide and sodium chloride compatible as expected, but also slight conversion to the reciprocal pair takes place. This can be seen in the polytherm Fig. 37 where, at the ternary eutectic, the solids KCl, NaCl and (KNa)I mixed crystals co-exist.[9] A rather flat minimum occurs in the pseudo-binary system NaCl-KBr at 610°C. and has the composition Br' 60%, K^+ 50%.[66] A method for calculating equilibrium constants in reciprocal salt-pairs by measurement of the temperature change on mixing reactants and products in varying proportions,[67] is based on the fact that maximum temperature change occurs when reactants and products are mixed, zero change when reactants and products are mixed

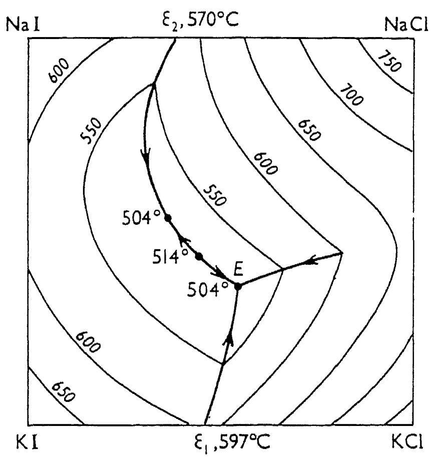


FIG. 37. POLYTHERMAL PROJECTION FOR THE RECIPROCAL SYSTEM NaCl-KI (ISOTHERMAL LINES DRAWN AT 50°C. INTERVALS)

in amounts corresponding to their equilibrium concentrations, and the opposite change when only products are mixed. The stable salt pair, temperature of measurement, and the equilibrium constant observed by this method are:-

NaCl-KBr	769°C.	1·75
NaCl-KI	777°C.	1·62

Bergman *et al.*[58] have made a detailed study of the system NaCl-K_2SO_4. Of the constituent binaries, NaCl-Na_2SO_4 and KCl-K_2SO_4 form simple eutectics at 628°C., 35%NaCl, 600°C., 42% K_2SO_4 respectively. The remaining binaries, KCl-NaCl and K_2SO_4-Na_2SO_4, form continuous series of mixed crystals, the critical solution points being 622° and 706°C. respectively. Considering this system as a square projection Bergman examined compositions representing the sides *i.e.* binaries, the diagonals, and sixteen internal cuts, and observed the existence of a binary compound tentatively assumed to be $3Na_2SO_4$, K_2SO_4 or Na_2SO_4,K_2SO_4, which was stable between 514° and 706°C. Earlier examination of this system by Jänecke had not revealed such a compound. Bergman observed one ternary eutectic and two transition points, temperatures and compositions of which are given in Table LXIV.

TABLE LXIV.- CHARACTERISTIC POINTS IN THE SYSTEM SODIUM CHLORIDE-POTASSIUM SULPHATE

Temp.°C.	Composition (mole-%)		
	Na_2Cl_2	K_2Cl_2	Na_2SO_4
514 (eutectic)	2·5	39	58·5
534 (transition)	13·5	25·5	61
538 (transition)	41·5	53	5·5

Potassium dichromate and sodium chloride are the stable salt-pair of the reciprocal couple and form a eutectic at 352°C., 17 mole-% Na_2Cl_2.[68] One transition and two other eutectics observed in this system are given in Table LXV. An inflexion at 340°C. on the crystallization branch of sodium dichromate in the binary system $K_2Cr_2O_7$-$Na_2Cr_2O_7$ indicates a polymorphic transition. Fig. 38 shows how the crystallization field of potassium dichromate increases with decreasing temperature. This property has been

TABLE LXV.- CHARACTERISTIC POINTS IN THE SYSTEM SODIUM CHLORIDE-POTASSIUM DICHROMATE

Temp.°C.	Composition (mole-%)		
350 (transition)	Na_2Cl_2 15·5	$K_2Cr_2O_7$ 81·5	K_2Cl_2 3
302 (eutectic)	Na_2Cl_2 5	$K_2Cr_2O_7$ 38·5	$Na_2Cr_2O_7$ 56·5
300 (eutectic)	Na_2Cl_2 5	$K_2Cr_2O_7$ 25	$Na_2Cr_2O_7$ 70

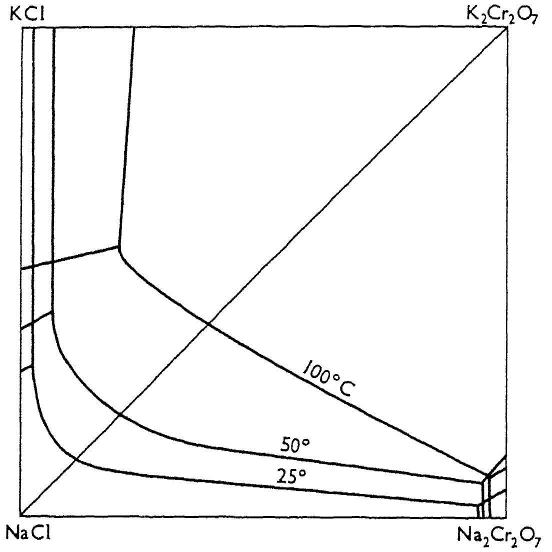


FIG. 38. ISOTHERMS FOR THE RECIPROCAL SYSTEM NaCl + $K_2Cr_2O_7$ SHOWING THE PERSISTENTLY SMALL FIELD OF SODIUM DICHROMATE

suggested as a basis for the industrial production of potassium dichromate by a cyclic method.[69] The behaviour of the quaternary reciprocal system NaCl-K_2SO_4-H_2O has been established (Mellor,II,689). Aqueous ammonia decreases the solubility of constituent salts and increases the stability of glaserite at the expense of the sodium sulphate decahydrate field. Addition of ammonia can thus be of value in effecting separation of salt mixtures.[70] The system NaCl-K_2CO_3-H_2O which has been examined optically and crystallographically,[71] is complicated by formation of several hydrates, and Fig. 39. gives the Löwenhertz projection of the isotherm at 25°C. Sodium chloride and potassium nitrate are the stable salt pair of the aqueous reciprocal system.[74] Eutectics are formed in each of the binary subsystems which lead to formation of two ternary eutectics. Its behaviour with respect to temperature is important since it forms the basis of a cyclic process for the manufacture of potassium nitrate, and the same principle may be applied to other systems, e.g. the production of potassium dichromate from sodium dichromate discussed above. The method may be illustrated by reference to the Jänecke square projection Fig. 40. If liquid of composition *o* is first evaporated at 100°C. it precipitates sodium chloride, eventually reaching E_1 along E_1a. If now the solution is cooled to 5°C. E_1 will lie deep within the potassium nitrate field, and since the solution at 100°C. contains more potassium nitrate than will the solution at 5°C., and sufficient water is added to prevent precipitation of sodium chloride, pure potassium nitrate will be precipitated on cooling to 5°C. After precipitation the liquid will be of composition *x* (known as 'nucleus solution')

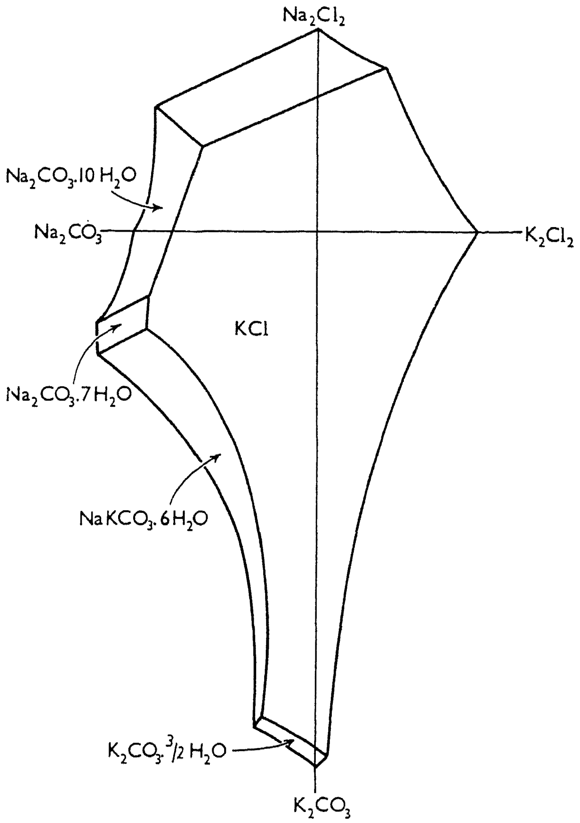

Na_2Cl_2
$Na_2CO_3.10H_2O$
Na_2CO_3
K_2Cl_2
KCl
$Na_2CO_3.7H_2O$
$NaKCO_3.6H_2O$
$K_2CO_3.{}^3/_2H_2O$
K_2CO_3

FIG. 39. 25°C. ISOTHERM FOR THE SYSTEM K_2CO_3-NaCl-H_2O (LOWENHERTZ PROJECTION)

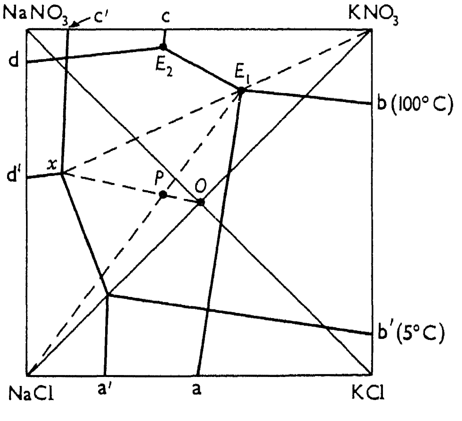
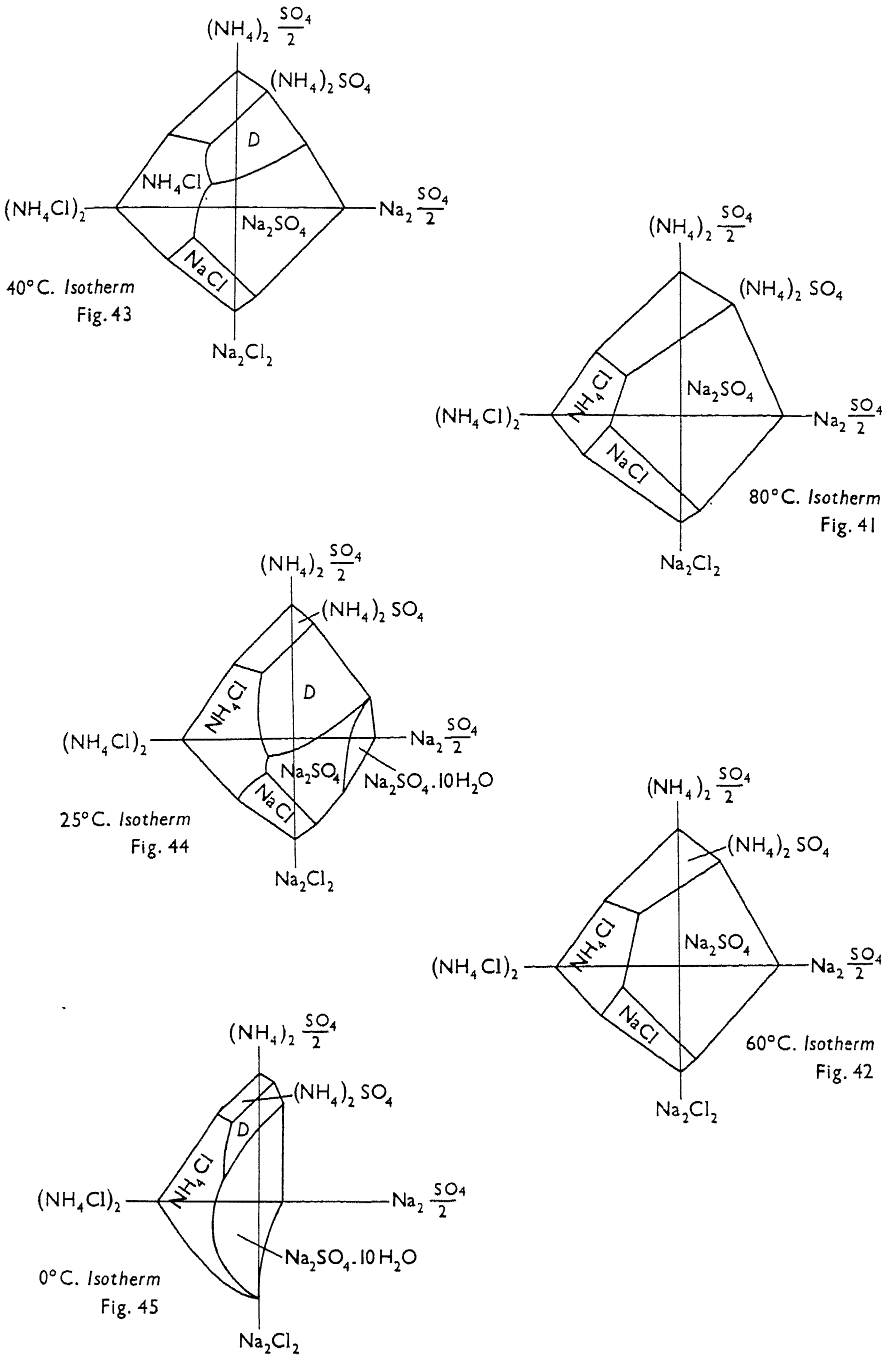

$NaNO_3$
c′
c
KNO_3
d
E_2
E_1
b (100° C)
d′
x
P
O
b′(5°C)
NaCl
a′
a
KCl

FIG. 40. ISOTHERMS AT 100°C. AND 5°C. FOR THE SYSTEM NaCl + KNO_3

and to this liquid is added the reactants sodium nitrate and potassium chloride in order to bring the composition of liquid to point *P*. Evaporation of water from this solution at 100°C. causes precipitation of sodium chloride and returns the liquid to composition E_1 and by then cooling the cyclic process is repeated. Aqueous systems $NaCl-KIO_3-H_2O$, $NaCl-KClO_4-H_2O$ are simple, these salt-pairs being stable. A cyclic separation of sodium nitrate and potassium perchlorate from aqueous solutions containing sodium chloride has been suggested[72] which is based on the same principle as the production of potassium nitrate discussed above. The double decomposition $NaCl + KClO_4 \rightleftharpoons NaClO_4 + KCl$ in water has been studied at 25°C. both by analysis of solids and by utilizing relations between activity coefficients and molalities obtained from the ternary subsystems.[73] The two methods are found to be in agreement. Solubility relations in this system have been obtained between 0° and 100°C.[78] The rate of crystallization has been found to influence the distribution of bromide in the crystallized phases of the system $KCl-NaBr-H_2O$ at low bromide concentrations.[13] Cornec and Krombach[75] have studied in detail the equilibrium between the chlorides, nitrates and sulphates of sodium and potassium in water over the range 0° to 90°C. The three regions studied were those in which sodium nitrate, sodium chloride and potassium nitrate are solid phases. Nine types of equilibrium occur in the sodium nitrate region and the corresponding eight transition temperatures have been obtained. With decreasing temperature the sodium nitrate field diminishes and finally disappears. Anhydrous sodium sulphate may coexist with sodium nitrate only above 55°C. and darapskite is stable above 3·4°C., but in more complex solutions the latter exists over a wider temperature range. Thirteen equilibria have been distinguished in the sodium chloride-saturated region. Anhydrous sodium sulphate exists above 11·6°C., darapskite above 3·4°C. and glaserite ($Na_2SO_4,2K_2SO_4$) above 1·3°C. Three inversion points occur at which all four components of a reciprocal salt pair coexist. Nine points of transition corresponding to ten equilibria are found in the potassium nitrate section. Anhydrous sodium sulphate is stable above 38°C. and darapskite above 3·4°C. while three points of inversion occur. The anhydrous quinary system $Na^+K^+||F'Cl'Br'I'$ has been studied by Bergman and Dombrovskaya.[76]

Systems Containing The Ammonium Ion.

Alkali halides ionize and become solvated when dissolved in liquid ammonia; vapour pressure and solubility measurements have confirmed the existence of the compound $NaCl,5NH_3$ stable below −10°C. (Mellor,II,554).[79,80] The solubility of sodium chloride in liquid ammonia containing dissolved sodium and the specific gravity and vapour pressure of such solutions have been studied in the range 0° to −20°C.[81] Because ammonium chloride is produced at the cathode during electrolysis of a solution of sodium chloride in liquid ammonia, the ternary system $NaCl-NH_4Cl-NH_3$ has been studied from −75°C. to 110°C. for ratios $NaCl:NH_4Cl$ of 2:1, 1:1, 1:2, 1:4 and 1:10.[82] Solubility relations in the system $NaCl-NH_4Cl-H_2O$ have been determined in the range −10°C. to 100°C.[33,83,84] The mutual solubility of salts in the systems $(NH_4)_2SO_3 + 2NaCl \rightleftharpoons 2NH_4Cl + Na_2SO_3$ and $NaCl + NH_4HSO_3 \rightleftharpoons NaHSO_3 + NH_4Cl$ has been studied, the former at 60° and 80°C. and the latter at 25° and 60°C. Results indicate that commercial production of sodium sulphite and ammonium chloride from sodium chloride, sulphur dioxide and ammonia is feasible.[85] The quaternary reciprocal system $NH_4Cl-Na_2SO_4-H_2O$ has been studied between 0° and 80°C.[86] Orthogonal projection of isotherms at 0°, 25°, 40°, 60° and 80°C. given in Figs. 41–45 show the behaviour of this system with respect to temperature. At 17·9°C. the sodium sulphate field vanishes and the double salt $Na_2SO_4,(NH_4)_2SO_4,4H_2O$ (*D* in Figs. 43–45) is said to appear below 59·3°C. in the ternary system of the two sulphates and water. Recovery of ammonia in the ammonia-soda process by conversion to ammonium chloride has led to a study at 15°C. of the conditions under which ammonium


$(NH_4)_2\frac{SO_4}{2}$
$(NH_4)_2SO_4$
D
NH_4Cl
$(NH_4Cl)_2$
$Na_2\frac{SO_4}{2}$
Na_2SO_4
NaCl
Na_2Cl_2
$Na_2SO_4.10H_2O$

40°C. *Isotherm*
Fig. 43

80°C. *Isotherm*
Fig. 41

25°C. *Isotherm*
Fig. 44

60°C. *Isotherm*
Fig. 42

0°C. *Isotherm*
Fig. 45

FIGS. 41–45. ISOTHERMS FOR THE SYSTEM $(NH_4)_2SO_4$-NaCl-H_2O (LÖWENHERTZ PROJECTIONS) and sodium carbonates and chlorides crystallize from solution.[87] The isotherm consists of four fields of crystallization corresponding to the four constituent salts, and the stable couple is ammonium chloride and sodium carbonate. Because of the presence of water vapour, ammonia and carbon dioxide above the system NaCl + NH_4HCO_3 + H_2O, this system is quinary and not quaternary, and knowledge of the composition of this system requires knowledge of the partial pressure of carbon dioxide above it. Experiment has shown that the equilibrium pressure above a saturated solution of ammonium bicarbonate is much higher than 1 atm. at ordinary temperatures, this pressure obtaining at about 3°C.[88] Hence studies carried out on this system under carbon dioxide at atmospheric pressure may not give accurate information on the phase behaviour but may be justified where they are applied to the ammonia-soda process at atmospheric pressure.[89-91] Application of higher pressures of carbon dioxide has been shown to increase the efficiency of production of sodium bicarbonate.[92,93] The influence of added potassium chloride on the equilibrium NaCl + $NaHCO_3 \rightleftharpoons NaHCO_3$ + NaCl and of ammonia and carbon dioxide on the composition of the aqueous system KCl-NaCl-NH_4Cl has also been studied.[94] The two aqueous reciprocal systems, $NH_4H_2PO_4$-NaCl-H_2O and $(NH_4)_2HPO_4$-NaCl-H_2O, have been studied at 0° and 25°C. In the former the solids $NH_4H_2PO_4$, NH_4Cl, NaCl, $NaH_2PO_4,2H_2O$ occur, $NaH_2PO_4,2H_2O$ and NH_4Cl coexisting at 0°C. but not at 25°C.[95] Five domains comprise the phase diagrams of the latter system,[96] the double salt $NaNH_4HPO_4$ occupying the largest area as shown in Fig. 46., the composition of invariant points

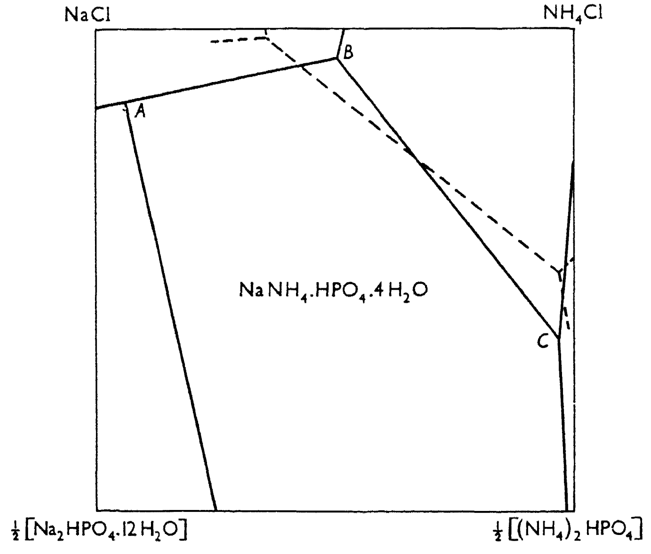


FIG. 46. ISOTHERMAL PROJECTIONS FOR THE SYSTEM NaCl + $(NH_4)_2HPO_4$ AT 25°C. (FULL LINE) AND 0°C. (BROKEN LINE)

being given in Table LXVI. Polythermal investigation of the system $NaNO_3$-NH_4Cl by means of cooling curves shows absence of double salts or mixed crystals.[97] Binary eutectics exist at 141° and 121°C. for NH_4Cl-$NaNO_3$ and NH_4NO_3-NaCl respectively, and ternary eutectics are found at 133°C. for

TABLE LXVI.- INVARIANT POINTS IN THE SYSTEM SODIUM PHOSPHATE-AMMONIUM CHLORIDE-WATER

Point	Isotherm Temp.°C.	Composition (g.-ions per 1000 moles H_2O)			
		Na^+	NH_4^+	HPO_4''	Cl'
A	0	-	-	-	-
	25	6·51	0·40	0·46	5·99
B	0	4·9	2·80	0·08	7·55
	25	4·34	4·67	0·23	8·55
C	0	0·30	10·1	2·65	0·51
	25	0·45	9·04	1·64	6·21

$NaCl$-$NaNO_3$-NH_4Cl, and at 112°C. for NH_4NO_3-$NaNO_3$-NH_4Cl. This system was investigated in detail in the neighbourhood of the ternary eutectics and Fig. 47. gives the projection of this section. At 20°C. the system $NaCl$-NH_4NO_3-H_2O has four crystallization fields corresponding to the constituent salts. The influence of added ammonia on this system has been studied[98] and is depicted in Fig. 48. which is a Lowenhertz projection at 20°C. The dotted lines show the influence of ammonia the concentrations of which are given (on the dotted lines) in moles per 100 g. of water. Since *A B* represents the junction between saturation surfaces of ammonium chloride and sodium nitrate it is possible to precipitate pure sodium nitrate from solutions of a certain composition by adding excess of ammonia. Likewise ammonium chloride may be precipitated by partially removing ammonia from the system.

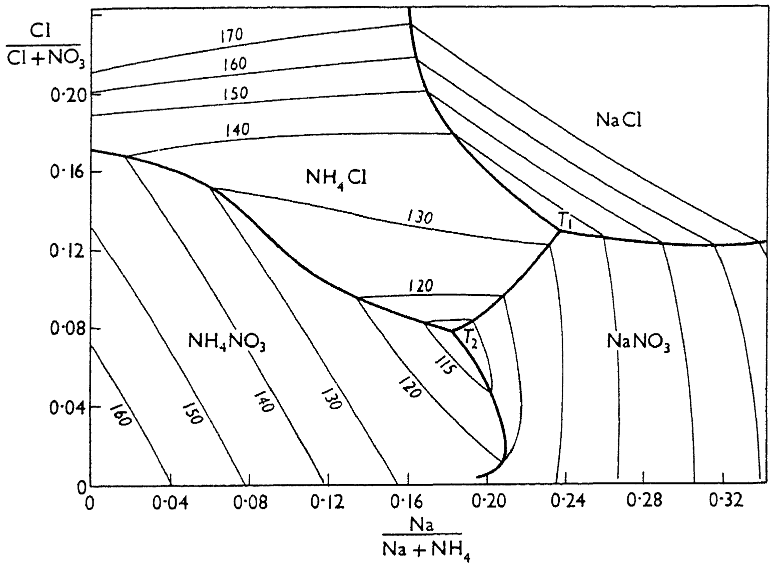


FIG. 47. THE AMMONIUM NITRATE CORNER OF A SQUARE POLYTHERMAL PROJECTION OF THE SYSTEM $NH_4NO_3 + NaCl$

Systems Containing Magnesium.

The tendency of a magnesium halide to form binary compounds of the type MgX_2,MX with the corresponding halide of an alkali metal M increases from bromide to fluoride and from lithium to potassium.[99] Thermal and X-ray analysis of the binary system sodium chloride-magnesium chloride has confirmed the existence of compounds $2NaCl,MgCl_2$ and $NaCl,MgCl_2$ observed

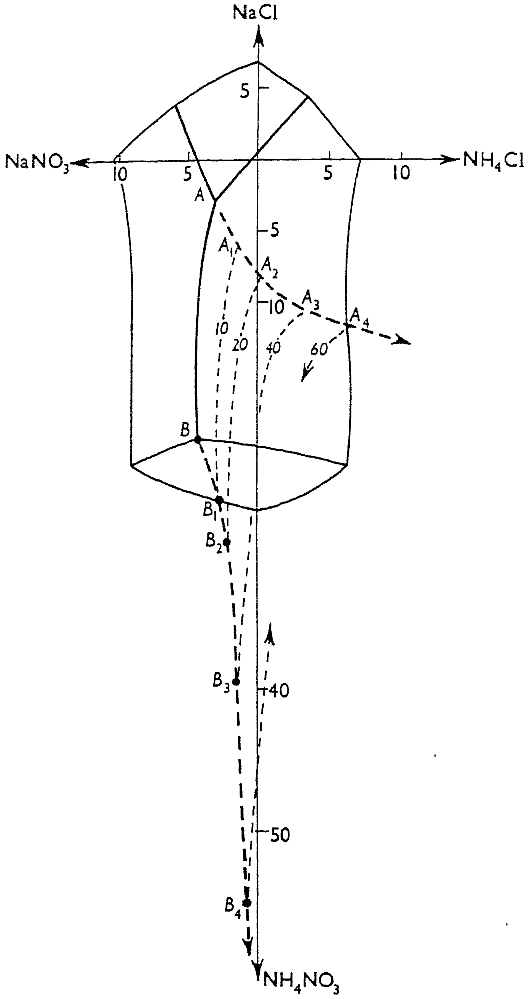


FIG. 48. INFLUENCE OF ADDED AMMONIA ON 20°C. ISOTHERM OF NH_4NO_3-NaCl-H_2O (LOWENHERTZ PROJECTION) CONCENTRATION OF SALTS MOLES/1000 GM. H_2O

earlier by Scholich (Mellor,IV,307). NaCl,$MgCl_2$ melts at 465°C. and 2NaCl, $MgCl_2$ at 485°C., and they form a eutectic at 450°C.[99] Solubility relations in the temperature range 10° to 200°C. have been obtained for the ternary system $MgCl_2$-NaCl-H_2O.[3,4,22,25,100,101] No double salts appear to be formed. At moderate temperatures up to about 250°C. sodium chloride, unlike potassium chloride, exhibits decreasing solubility with increasing magnesium chloride concentration, and this fact may be used to separate sodium chloride from concentrated solutions containing potassium and magnesium chlorides.[101] At higher temperatures, while the behaviour of sodium chloride remains unchanged, the concentration of potassium chloride becomes nearly independent of that of magnesium chloride.[100] Solubility and density determinations in the system NaCl-$Mg(NO_3)_2$-H_2O and in its ternary subsystems enabled isotherms to be constructed at 15°, 25° and 50°C.[22] The stable salt-pair below 50°C. is $Mg(NO_3)_2,6H_2O$ + NaCl and increase of temperature from 15° to 50°C. increases the fields of sodium chloride at the expense of sodium nitrate and increases that of $MgCl_2,6H_2O$ at the expense of the $Mg(NO_3)_2,6H_2O$ field. In the neighbourhood of 50°C. there occurs an inversion point (not determined), at which all four constituent salts coexist. Solubility and photomicrographic examination of the system $NaHCO_3$-$NaCl$-$MgCO_3$-H_2O at 50°C., under 185 mm. partial pressure of carbon dioxide, has shown the existence of a triple salt $NaCl, Na_2CO_3, MgCO_3$.[102] The temperature and pressure at which this study was made were chosen to simulate conditions prevailing in the ammoniation step of the Solvay process; formation of this salt thus represents an unavoidable loss of sodium chloride and sodium carbonate from the process. Because of the preponderance of sodium and magnesium chlorides and sulphates in sea water the system $MgSO_4$-$NaCl$-H_2O has been the subject of much study.[103-122] Repetition of the work of van't Hoff and Meyerhoffer (Mellor, IV, 347) has led to reassignment of some invariant points with consequent alterations in shapes of crystallization surfaces. The hydrates $MgSO_4,4H_2O$ and $MgSO_4,5H_2O$, obtained at 25°C. by Takegami[109] were not observed by Blasdale[110] or by later investigators[103,105-106] and were considered by van't Hoff to be metastable at 25°C. Though van't Hoff considered kieserite ($MgSO_4,H_2O$) to possess a small field of stability at 25°C., Blasdale failed to observe it and considers it metastable at 25°C.[110] Great difficulty has been experienced in obtaining true equilibrium in saturated solutions of this system at 25°C.[113] and this is probably responsible, in part at least, for these conflicting observations on the form of the 25°C. isotherm. The complete phase diagram obtained by Blasdale[110] is given as a Lowenhertz projection in Fig. 49, composition of the lettered points being given in Table LXVII.

TABLE LXVII.- CHARACTERISTIC POINTS IN THE SYSTEM SODIUM CHLORIDE-MAGNESIUM SULPHATE-WATER AT 25°C.

Solid Phase	Composition of solution, g./100 g. of water			
	$MgSO_4$	Na_2SO_4	$NaCl$	$MgCl_2$
A. $MgSO_4,7H_2O$	36·39	-	-	-
B. $Na_2SO_4,10H_2O$	-	27·93	-	-
C. $NaCl$	-	-	35·63	-
D. $MgCl_2,6H_2O$	-	-	-	54·97
E. $MgSO_4,7H_2O$, astrakanite	32·07	19·68	-	-
F. $Na_2SO_4,10H_2O$, astrakanite	25·36	27·09		
G. $Na_2SO_4,10H_2O$, Na_2SO_4		21·68	18·82	
H. Na_2SO_4, $NaCl$		9·81	32·16	
I. $NaCl$, $MgCl_2,6H_2O$	-	-	-	54·87
J. $MgCl_2,6H_2O$, $MgSO_4,6H_2O$	3·61	-	-	54·01
K. $MgSO_4,6H_2O$, $MgSO_4,7H_2O$	6·37	-	-	40·74
L. Na_2SO_4, $Na_2SO_4,10H_2O$ astrakanite	7·71	18·67	15·50	-
M. Na_2SO_4, $NaCl$, astrakanite	12·59	1·01	29·67	-
N. $MgSO_4,7H_2O$, $NaCl$, astrakanite	12·03	-	9·79	20·47
O. $MgSO_4,7H_2O$, $MgSO_4,6H_2O$, $NaCl$	6·53	-	2·20	39·94
P. $MgSO_4,6H_2O$, $MgCl_2,6H_2O$, $NaCl$	2·53	-	0·18	53·88

In Table LXVIII are given compositions obtained independently by Blasdale,[110] Pel'sh[114] and Rose[113] for three invariant points. The system has been examined at 35°C.,[25] and the 55°C. isotherm has revealed in addition to astrakanite (I) the double salts $3Na_2SO_4,MgSO_4$ (II), $Na_2SO_4,MgSO_4,2H_2O$ (III) and kieserite (IV).[115] Also present are $NaCl$ (V), Na_2SO_4 (VI), $MgSO_4$ (VII), $MgCl_2, 6H_2O$ (VIII). Table LXIX gives the compositions of solution and solid phases

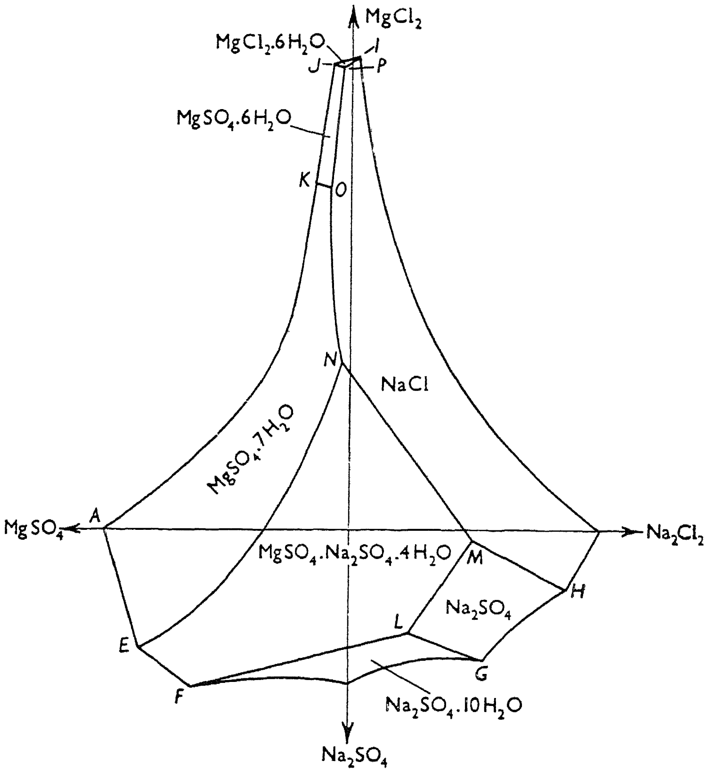

MgCl₂
MgCl₂.6H₂O
I
J
P
MgSO₄.6H₂O
K
O
N
NaCl
MgSO₄.7H₂O
A
MgSO₄
Na₂Cl₂
MgSO₄.Na₂SO₄.4H₂O
M
H
Na₂SO₄
L
E
G
F
Na₂SO₄.10H₂O
Na₂SO₄

FIG. 49. 25°C. ISOTHERM FOR THE SYSTEM NaCl + $MgSO_4$ + H_2O (LOWENHERTZ PROJECTION)

TABLE LXVIII.- INVERSION POINTS IN THE SYSTEM SODIUM CHLORIDE-MAGNESIUM SULPHATE-WATER

Point		Composition (moles per 1000 moles water)		
		Blasdale	Pel'sh	Rose
L	Na_2Cl_2	23·8	17·46	26·3
	Na_2SO_4	23·8	29·69	26·0
	$MgSO_4$	11·5	20·44	11·6
N	Na_2Cl_2	15·0	12·8	-
	$MgSO_4$	18·05	43·98	-
	$MgCl_2$	39·2	16·39	-
O	Na_2Cl_2	3·38	4·24	-
	$MgSO_4$	9·75	11·38	-
	$MgCl_2$	76·2	67·36	-

at the eight ternary eutectics.

The isotherm at 105°C. shows that at this temperature astrakanite is no longer stable, but there exists a new double salt $2Na_2SO_4,2MgSO_4,5H_2O$[112,116] in addition to $3Na_2SO_4,MgSO_4$. Polythermal investigations of this system have been made down to −20°C.[111,114,117] At 0°C. NaCl, $Na_2SO_4,10H_2O$, $MgSO_4,7H_2O$,

TABLE LXIX.- TERNARY EUTECTICS IN THE SYSTEM SODIUM CHLORIDE-MAGNESIUM SULPHATE-WATER

Solid Phases	Composition of solution (mole-%)	
	Mg^{++}	SO_4''
I II VI	37	70
II V VI	29·62	25·1
I II V	43·42	23·83
III V VII	92	68
III IV VII	96	50
II III V	73·56	23·80
III IV V	94·47	18·34
IV V VIII	99·37	0·83

$MgCl_2,6H_2O$ coexist,[103] and at -7·75°C. $NaCl,2H_2O$ becomes stable, the solution being saturated with $NaCl,NaCl,2H_2O,Na_2SO_4,10H_2O,MgSO_4,7H_2O$.[114] The tendency of this system to exhibit metastability can be illustrated by the fact that a solution saturated with respect to $NaCl,Na_2SO_4,10H_2O,MgSO_4,7H_2O$ may be warmed to 13·9°C. without formation of astrakanite, though the latter is known to be stable above 5·85°C.[114] and promoters of crystallization have been used in an attempt to avoid such behaviour.[104] Vapour pressures above this system have been measured at 25°C. and 35°C. in the region of halide crystallization, at 35°C. in the region saturated with $Na_2SO_4,10H_2O$[118] and in stable and metastable regions.[119] Geochemical applications of this system are illustrated by efforts made to simulate natural conditions during isothermal evaporation,[120] and by the study of lake brines.[103,105,111,121]

The ternary system $NaCl$-KCl-$MgCl_2$ has been examined by Bergman,[76] Jänecke[123] and Scholich.[124] The latter obtained evidence for three binary compounds, $MgCl_2,NaCl$, $MgCl_2,KCl$ and $MgCl_2 2NaCl$, evidence for the latter being indirect. Eutectics are formed in the systems $KCl,MgCl_2$-$MgCl_2$ and $KCl,MgCl_2$-KCl and the whole system may be regarded as two systems (*A*) $NaCl$-$MgCl_2$-$KCl,MgCl_2$ and (*B*) $NaCl$-KCl-$KCl,MgCl_2$. System *A* contains five surfaces of crystallization belonging to $NaCl,MgCl_2$ and three double salts, two transition points and one eutectic. System *B* contains one eutectic comprising the double salt and two mixed crystal phases of $NaCl + KCl$. Other work confirms three ternary eutectics[125] while Jänecke, confirming the formation of $KCl,MgCl_2$ and $2NaCl,MgCl_2$, found a double salt $3NaCl,MgCl_2$ but no evidence for $MgCl_2,NaCl$. The polytherm obtained by Jänecke is shown in Fig. 50. as a triangular projection and from this it can be seen that $3NaCl,MgCl_2$ melts incongruently (since the point corresponding to this composition is not within the crystallization field of the salt) and that sodium chloride + potassium chloride mixed crystals have an upper consolute temperature of 615°C. Interest in the naturally occurring system $NaCl$-KCl-$MgCl_2$-H_2O has led to extensions of earlier work by van't Hoff and Meyerhoffer (Mellor,IV,307-9). Solubility isotherms at 0°C.,[126] 25°C.,[127] 100°C.[3] and extension up to 265°C.[62,128] have led to a method for extraction of potassium chloride from sylvite. By dissolving the mineral in water at 100°C. and slowly cooling to 10°C. pure potassium chloride is deposited and further deposition may be obtained by salting out with sodium chloride. Optimum conditions have been obtained for extraction of pure potassium and magnesium chlorides at various temperatures from liquors representing the system.[129,130] Methods for graphical representation of this system have been discussed.[131,132] Many workers have investigated the quinary system $Mg^{++},K^+,Na^+||Cl',SO_4''$-$H_2O$. Solubility isotherms have been determined at temperatures between 25°C. and 100°C.,[133-139] usually with the system saturated by one or more salts. The isotherm at 25°C. shown in Fig. 51. is simplified in the magnesium chloride region of

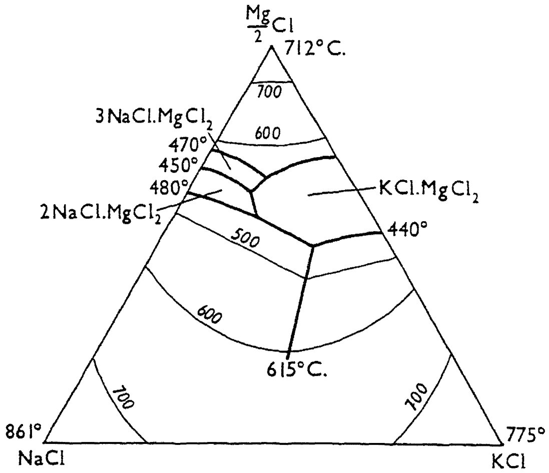


FIG. 50. POLYTHERM FOR THE SYSTEM KCl-$MgCl_2$-NaCl

which greater detail is given in Fig. 52. In Fig. 51 the six salts form corners of a regular triangular prism from which the water content has been eliminated by plotting only the concentrations of components in the dissolved salts. Thus in Figs. 51 and 52 and Table LXX

$$z_2 = \frac{\tfrac{1}{2}Mg}{Na + K + \tfrac{1}{2}Mg} \quad z_3 = \frac{K}{Na + K + \tfrac{1}{2}Mg} \quad z_4 = \frac{Cl}{\tfrac{1}{2}SO_4 + Cl}$$

Prism corners then represent saturated solutions of each dissolved salt, the square faces represent quaternary reciprocal systems and the equilateral triangles form quaternary systems having a common anion. Table LXX gives composition, formulae, and mineralogical names of the solid phases together with letters indicating their positions in Fig. 51.

TABLE LXX.- CONSTITUENTS IN THE SYSTEM Mg^{++}, K^+, $Na^+||Cl^-$, SO_4^{--}-H_2O

Formula	Mineralogical name	Co-ordinates			Indicated by
		z_2	z_3	z_4	
Na_2SO_4	thenardite	0	0	0	*A*
$Na_2SO_4,10H_2O$	mirabilite	0	0	0	*A*
$MgSO_4,H_2O$	kieserite	1	0	0	*B*
$MgSO_4,6H_2O$	hexahydrate	1	0	0	*B*
$MgSO_4,7H_2O$	reichardite	1	0	0	*B*
K_2SO_4	-	0	1	0	*C*
NaCl	halite	0	0	1	*P*
KCl	sylvite	0	1	1	*R*
$Na_2SO_4,MgSO_4,4H_2O$	astrakanite	½	0	0	D_1
$MgCl_2,6H_2O$	bischofite	1	0	1	*Q*
$Na_2SO_4,2K_2SO_4$	glaserite	0	⅔	0	D_2
$K_2SO_4,MgSO_4,6H_2O$	picromerite	½	½	0	D_3
$K_2SO_4,MgSO_4,2H_2O$	leonite	½	½	0	D_3
$KCl,MgCl_2,6H_2O$	carnallite	⅔	⅓	1	D_4
$KCl,MgSO_4,3H_2O$	kainite	⅔	⅓	⅓	T_1

Other geometrical constructions have been devised to represent more clearly the particular relationships within the system.[136,140,141,144] Metastability is

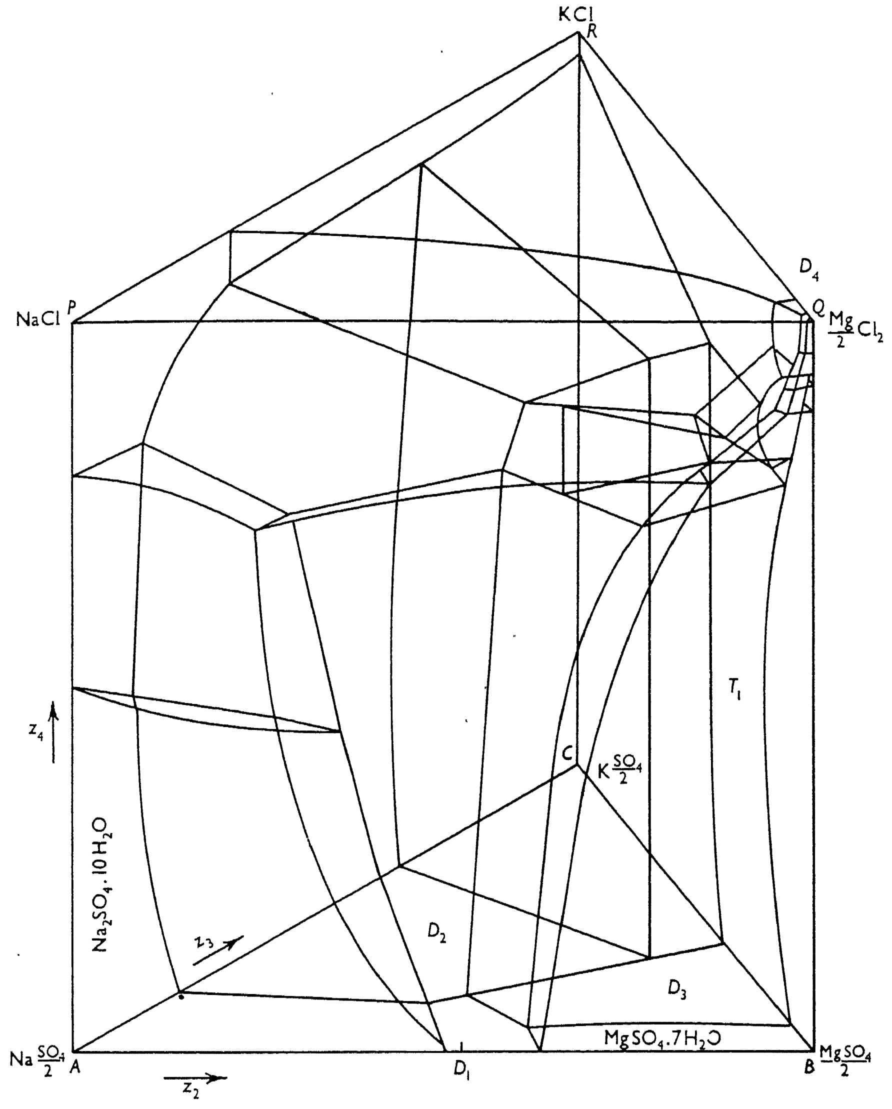

KCl
R
D_4
Q
$\frac{Mg}{2}Cl_2$
NaCl
P
z_4
$Na_2SO_4.10H_2O$
T_1
C
$K\frac{SO_4}{2}$
D_2
D_3
z_3
$MgSO_4.7H_2O$
$Na\frac{SO_4}{2}$
A
D_1
B
$\frac{MgSO_4}{2}$
z_2

FIG. 51. 25°C. ISOTHERM FOR THE QUINARY SYSTEM $Na^+K^+Mg^{++}||Cl'SO_4''-H_2O$

$$z_2 = \frac{\frac{1}{2}Mg}{Na + K + \frac{1}{2}Mg} \quad z_3 = \frac{K}{Na + K + \frac{1}{2}Mg} \quad z_4 = \frac{Cl}{SO_4 + Cl}$$

easily attained in this system. For example, it has been shown that precipitated sodium sulphate, potassium sulphate and glaserite are able to remove magnesium sulphate from solutions unsaturated with the latter.[142] By adding sodium chloride to glaserite solutions in presence of potassium chloride and magnesium sulphate at 98°C. thenardite is precipitated and carries with it magnesium sulphate, reducing the concentration of the latter from 5·5 mole/1000 moles H_2O to 1·2 moles/1000 moles H_2O, $MgSO_4$ appearing quantitatively in the solid. Theoretically magnesium sulphate is precipitated as van't Hoffite,

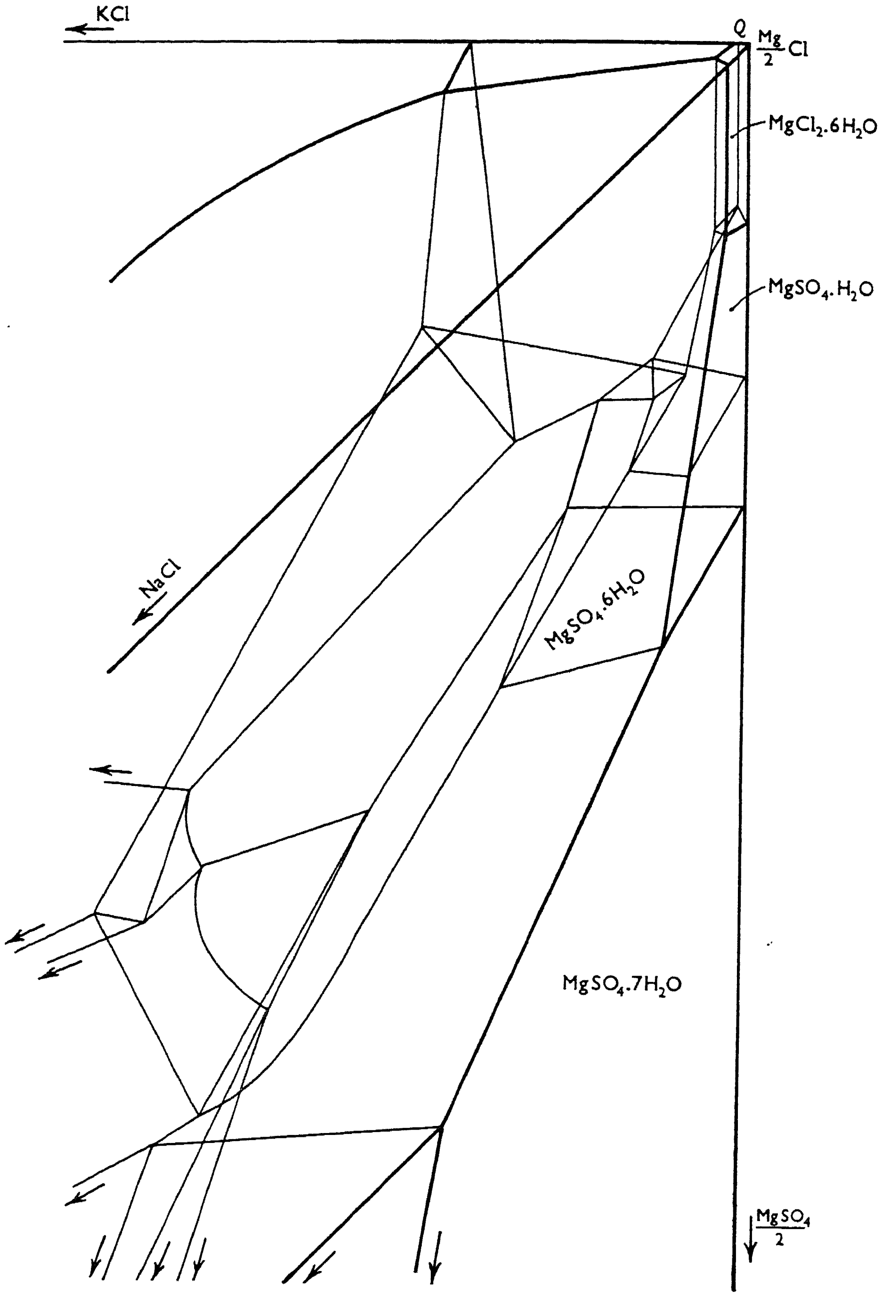

KCl
Q
$\frac{Mg}{2}$Cl
MgCl$_2$.6H$_2$O
MgSO$_4$.H$_2$O
NaCl
MgSO$_4$.6H$_2$O
MgSO$_4$.7H$_2$O
$\frac{MgSO_4}{2}$

FIG. 52. DETAIL OF MAGNESIUM CHLORIDE CORNER (BOLD LINES ARE SITUATED ON PRISM SURFACES)

$MgSO_4,3Na_2SO_4$, only at concentrations above 6 moles $MgSO_4$/1000 moles H_2O. The normally coarse thenardite crystals precipitated are transformed to fine crystals, and this is attributed to strain in the crystal lattice resulting from solid solution of magnesium sulphate in thenardite. Similar phenomena occur when potassium sulphate is used instead of glaserite. Metastability has been studied during isothermal evaporation[143] and in the presence of sodium chloride as a saturating phase[139] and polytherms obtained in regions saturated with sodium chloride[134] and potassium chloride.[133] Bergman, and later Jänecke, studied equilibrium between potassium, sodium, and magnesium chlorides and sulphates. Jänecke,[123] considering the system as a triangular prism, examined by freezing point measurements the quaternary subsystems bounding the prism and the diagonal cut representing K_2Cl_2-Na_2Cl_2-$MgSO_4$. The system is complicated by formation of the double salts discussed earlier for the ternary systems (Fig. 50) and the polythermal diagonal cut K_2Cl_2-Na_2Cl_2-$MgSO_4$. Fig. 53. shows the double salt of potassium chloride and magnesium sulphate over a limited region.

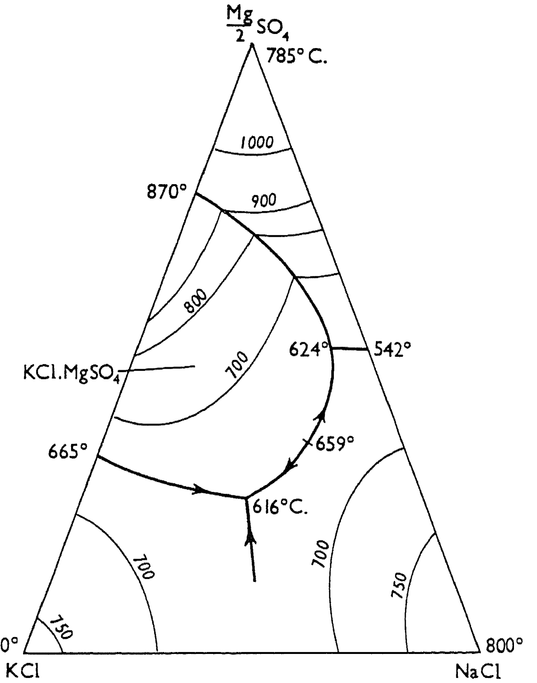


FIG. 53. DIAGONAL SECTION REPRESENTING THE SYSTEM KCl-NaCl-$MgSO_4$, THROUGH A REGULAR TRIANGULAR PRISM REPRESENTING THE SYSTEM $K^+Na^+Mg^{++}||Cl'SO_4''$

Systems Containing Calcium, Strontium, Barium.

Sodium chloride, unlike chlorides of potassium, rubidium and caesium, forms no compound with calcium chloride.[154] Lantsberry and Page[145] observed no eutectic arrest in their cooling curves and concluded that NaCl-$CaCl_2$ forms a continuous series of solid solutions with a minimum at 505°C. and 72·5 mole-% $CaCl_2$. It appears from the measured m.p. of their components that they contained considerable impurity. Other workers have observed a similar minimum, 506°C. and 53 mole-% $CaCl_2$,[124] 501°C. and 46 mole-% $CaCl_2$,[146] but conclude that it is a eutectic point, there being little or no solid solution. The compound 4NaCl,$CaCl_2$ reported by Menge has not been confirmed. No compound is reported between sodium chloride and calcium fluoride. M.p. measurements and analysis of solids enabled the polythermal diagram Fig. 54. to be obtained.[63] The composition and temperatures of the lettered points

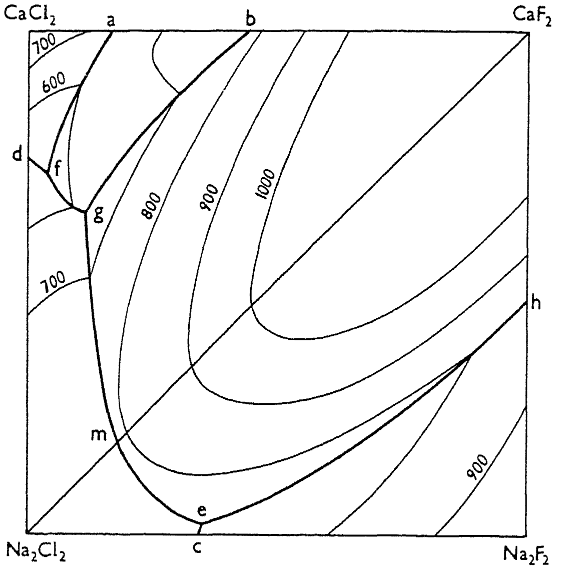


FIG. 54. POLYTHERMAL PROJECTION OF THE RECIPROCAL SYSTEM CaF_2-NaCl

are given in Table LXXI.

TABLE LXXI.- SOLID PHASES IN THE SYSTEMS OF SODIUM CHLORIDE WITH ALKALINE EARTH METAL HALIDES

Point	Solid Phases	Composition mole-%	Temp.°C.
a	$CaCl_2, CaF_2 + CaCl_2$	CaF_2 18·6	664
b	$CaF_2 + CaCl_2, CaF_2$	CaF_2 44	755
c	NaCl + NaF	NaF 37	680
d	$CaCl_2$ + NaCl	$CaCl_2$ 58·3	520
e	CaF_2 + NaF + NaCl	F_2 34·6 Ca 1·25	686
f	$CaCl_2, CaF_2 + CaCl_2$ + NaCl	F_2 3·5 Ca 73	506
g	$CaCl_2, CaF_2$ + NaCl + CaF_2	F_2 22 Ca 63·5	609
h	$CaF_2 + NaF_2$	CaF_2 32·5	810
m	CaF_2 + NaCl	F_2 19·6 Ca 19·6	778

The stable salt pair $CaSO_4$-NaCl behaves as a binary system forming a eutectic at 720°C. and 31 mole-% $CaSO_4$[147] and thus resembles the corresponding strontium and barium systems.[147,148] Isotherms at 50°C. and 94·5°C.[149] show that in the system NaCl-$CaCl_2$-H_2O the solids present are NaCl and $CaCl_2, 2H_2O$ at 0°C. NaCl,$2H_2O$, though stable in water up to 0·15°C., is not observed to be present owing to lowering of its freezing point by calcium chloride.[150] From Fig. 55. it can be seen that the main crystallization branch corresponds to solutions in equilibrium with solid sodium chloride and by comparison with the systems $CaCl_2$-KCl-H_2O and $CaCl_2$-$MgCl_2$-H_2O the other branch is inferred to represent solutions in equilibrium with $CaCl_2, 6H_2O$. It requires, however, so little sodium chloride to saturate this system that experimental verification of this branch has not been obtained.[150] The equilibrium 2NaCl + Ca $\rightleftharpoons$ $CaCl_2$ + 2Na has been determined from both sides to be the same. A miscibility gap appears in the region 16 to 98·5% $CaCl_2$.[151]

Refs. p. 916

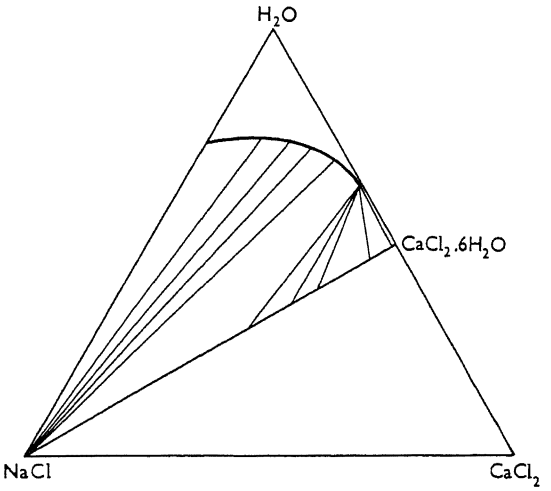


FIG. 55. ISOTHERM AT 0°C. FOR THE TERNARY SYSTEM $CaCl_2$-NaCl-H_2O

Displacement of this equilibrium to the right by lead and antimony has been examined.[152] Knowledge obtained by investigation of equilibria in the system $CaSO_4$-NaCl-H_2O, has been applied to isolation of gypsum from saliferous rock by forcing water through the rock.[153] The ternary system NaCl-$CaCl_2$-KCl has been investigated by Scholich.[124,155] A double salt, KCl,$CaCl_2$, effectively divides the system into two. In the one part there is a eutectic point at which $CaCl_2$, NaCl and KCl,$CaCl_2$ coexist. In the second part of the system KCl + NaCl + KCl,$CaCl_2$ double salt and (KNa)Cl mixed crystals are the solid phases. Isotherms at 18°, 50° and 95°C. have been obtained for the quaternary system $CaCl_2$-KCl-NaCl-H_2O.[156] The only double salt formed is KCl,$CaCl_2$, stable above 37·80 ± 0·05°C. There are two invariant points at 26·90 ± 0·05°C. and 43·3 ± 0·05°C. at which coexist the solid phases $CaCl_2$, $6H_2O$ + $\alpha CaCl_2,4H_2O$ + KCl + NaCl and $\alpha CaCl_2,4H_2O$ + $CaCl_2$,KCl + $CaCl_2,2H_2O$ + NaCl respectively. A triple salt $Ca(OCl)_2$,NaOCl,NaCl is reported to be formed in the system $Ca(OCl)_2$-NaCl-H_2O at temperatures below approximately 0°C.[157] The seven component system $Na^{+}Ca^{++}||CO_3{''}SO_4{''}Cl{'}$-$CO_2$-$H_2O$ has been studied. Determination of solubilities of calcium carbonate and calcium sulphate in water containing up to 2% of sodium chloride under pressures of carbon dioxide ranging from 0·009 to 1·00 atmosphere, has made possible some predictions about solution of calcite and gypsum in river waters.[158]

Barium chloride and sodium chloride form a simple eutectic at 656°C. and 40 mole-% $BaCl_2$,[146] or 648°C. and 51·5 mole-% $BaCl_2$.[159] No compounds are formed but there appears to be some solid solution (5–10 mole-% $BaCl_2$ is dissolved in NaCl at the eutectic point).[146] The aqueous system $BaCl_2$-NaCl-H_2O has been studied at 20°C. as part of the quaternary system $Ba(ClO_3)_2$ + NaCl + H_2O, in which it has been shown that $Ba(ClO_3)_2$ + NaCl are the stable couple.[38] Calcium and strontium sulphates are more soluble in liquid sodium chloride at 801°C. than in barium sulphate, which forms a eutectic at 741°C. containing 20 mole-% of sodium chloride.[148] Sodium chloride plus barium nitrate forms one of the simplest examples of a system intermediate between reversible-reciprocal and irreversible systems, since no compounds, solid solutions or polymorphous transitions occur.[160] The four fields of crystallization join at two points details of which are given in Table LXXII.

TABLE LXXII.- SOLID PHASES IN THE SYSTEM SODIUM CHLORIDE-BARIUM NITRATE

Solid Phases	Temp. °C.	Composition of liquid phase (mole-%)		
		$(NaNO_3)_2$	$(NaCl)_2$	$Ba(NO_3)_2$
$NaNO_3 + NaCl + Ba(NO_3)_2$	280	81	7·5	11·5
$NaCl + Ba(NO_3)_2 + BaCl_2$	405	1	38	61

Interest in preparation of barium chloride from barytes has led to a study of the equilibrium $Ba(SH)_2 + 2NaCl \rightleftharpoons BaCl_2 + 2NaSH$ by examining solubility relations in the ternary subsystems at 20°C.[42] In order to obtain maximum precipitation of barium chloride the initial solution must contain 35% $Ba(SH)_2$ and this may be prepared by saturating with hydrogen sulphide a solution containing 17·9% barium hydrosulphide and 14% barium sulphide. By this process 340 kg. of barium chloride may be prepared from one ton of barytes. The reciprocal system NaCl + $BaCO_3$ has been examined from its constituent binaries and from fourteen internal planes, two of which are diagonals.[159] Characteristics of the binaries and diagonals are given in Table LXXIII.

TABLE LXXIII.- CHARACTERISTIC POINTS IN THE SYSTEM SODIUM CHLORIDE-BARIUM CARBONATE

System	Characteristics (composition in mole-%)
Na_2CO_3-$BaCO_3$	Eutectic at 686°C. and 37% $BaCO_3$. Polymorphous transitions $\alpha \rightarrow \beta$ $BaCO_3$ and $\beta \rightarrow \gamma$ $BaCO_3$ at 811°C. and 982°C.
NaCl-$BaCl_2$	Eutectic at 648°C. and 51·5% $BaCl_2$.
$BaCl_2$-$BaCO_3$	Eutectics at 814°C. and 734°C. and 24% and 47% $BaCO_3$ respectively. Compound $2BaCl_2,BaCO_3$ m.p. 827°C.
NaCl-$BaCO_3$	Eutectic at 696°C. and 44% $BaCO_3$. Polymorphous transition $\beta \rightarrow \gamma$ $BaCO_3$ at 811°C. with 68% $BaCO_3$.
Na_2CO_3-$BaCl_2$	Unstable couple, diagonal passes through crystallization fields of $BaCO_3$, NaCl and $2BaCl_2,BaCO_3$, intersecting these branches at 566°, 632°, 684°C. with 21·5%, 71%, 81% $BaCl_2$ respectively.

The diagonal NaCl-$BaCO_3$ divides the system into two ternaries: (i) NaCl-$BaCO_3$-Na_2CO_3 and (ii) NaCl-$BaCl_2$-$BaCO_3$. In (i) the melt solidifies at the ternary eutectic 562°C., but (ii) is further divided by the adiagonal NaCl-$2BaCl_2,BaCO_3$ into two systems, $BaCl_2$-NaCl-$2BaCl_2,BaCO_3$ having a ternary eutectic at 618°C., and $BaCO_3$-NaCl-$2BaCl_2,BaCO_3$ with a ternary eutectic at 628°C. Isotherms between 18°C. and 115°C. for the ternary system NaCl-$SrCl_2$-H_2O show that no double salts are formed,[161] $SrCl_2,6H_2O$ is stable below 59·5 ± 0·5°C. and $SrCl_2,H_2O$ above this temperature. No double salts are formed in the system NaCl-KCl-$SrCl_2$-H_2O, and the transition $SrCl_2,6H_2O \rightarrow SrCl_2,H_2O$ occurs at 56·0 ± 0·5°C.[161] A simple eutectic is formed between sodium chloride and strontium sulphate; it melts at 738°C. and contains 24 mole-% of strontium sulphate.[148] Two compounds are formed in the system KCl-$SrCl_2$: $2KCl,SrCl_2$ melts at 597°C. and forms rhombic crystals, and $KCl,2SrCl_2$ melts at 638°C. and is thought to be monoclinic.[124] With sodium chloride, $KCl,2SrCl_2$ forms a pseudo-binary thus dividing the ternary NaCl-KCl-$SrCl_2$ into two partial systems. Breakdown of sodium chloride-potassium chloride solid solutions does not commence above the lowest eutectic; thus there are four surfaces of crystallization corresponding to $KCl,2SrCl_2$, 2KCl, $SrCl_2$, $SrCl_2$,KCl-NaCl solid solution.[124]

The compound $NaCl,BaCl_2$ reported by Guntz (Mellor,IV,307) has not been observed either in the binary system or in any ternary system such as $NaCl$-$BaCl_2$-$CaCl_2$.[146] By thermal analysis this ternary system has been shown to be simple. Three binary eutectic lines converge at a ternary eutectic at 453°C. of composition (mole-%) $BaCl_2$ 16, $CaCl_2$ 47, NaCl 37,[146] in good agreement with later work.[162] A transition α-$BaCl_2 \rightarrow \beta$-$BaCl_2$ occurs at 927°C.[146] in the binary $CaCl_2$-$BaCl_2$, but does not appear to have been observed in the system containing sodium chloride, where a transition line would be expected. The corresponding transition line has been examined in the system $NaCl$-$BaCl_2$-$SrCl_2$ as far as point b[9] in Fig. 56. Beyond this point the relatively small quantity of barium chloride in the mixture makes observation of the transition too difficult.[88] Mixtures of strontium and barium chlorides form a continuous series of solid solutions with a minimum m.p., whilst sodium chloride is not miscible in either strontium or barium chloride forming eutectics E_1 and E_2 (Fig. 56) which, in the ternary system, meet at a minimum of 560°C.[163] Thus a liquid of composition x, (Fig. 56), on cooling first deposits mixed crystals α-$BaCl_2$ + $SrCl_2$, at m there is a temperature arrest while the transition α-$BaCl_2 \rightarrow \beta$-$BaCl_2$ is completed, thereafter $SrCl_2$ + β-$BaCl_2$ mixed crystals are deposited until the eutectic line E_1E is reached whereupon sodium chloride is also deposited until finally the whole system freezes at the composition of eutectic E.

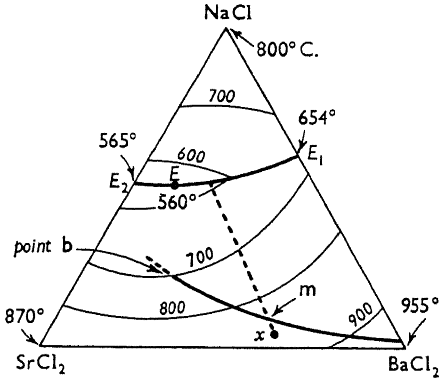


FIG. 56. POLYTHERM FOR THE SYSTEM $NaCl$-$SrCl_2$-$BaCl_2$ SHOWING PROGRESS OF CRYSTALLIZATION ON COOLING IN A LIQUID OF COMPOSITION x

Knowledge of the phase relationships in the system $CaCl_2$-$NaCl$-$MgCl_2$-H_2O has been applied to observed changes in composition of certain salt-water lakes over a period of sixty years.[164] Results indicate that the deposited sodium chloride is of high purity with respect to calcium and magnesium. It is predicted that deposition of tachydrite is improbable but bischofite may be deposited with sodium chloride after some years. Other similar geochemical studies have been made. Characteristics of the quinary system $Ca^{++}Sr^{++}K^{+}$-Na^{+} || Cl'-H_2O are largely determined by the quaternary formed by excluding sodium chloride.[167] Sodium chloride is only slightly soluble in solutions saturated with respect to the other compounds as shown in Table LXXIV. Eight crystallization fields exist between 18° and 114°C. $SrCl_2$ (I), α-$CaCl_2,4H_2O$ (II), $CaCl_2,6H_2O$ (III) solid solution $(CaSr)Cl_2,6H_2O$ (IV), $SrCl_2,2H_2O$ (V), KCl (VI), $KCl,CaCl_2$ (VII), NaCl (VIII).

Isotherms have been determined at 25°C. intervals from the freezing point, for the system $NaCl$-KCl-$CaCl_2$ in the presence of a constant amount of magnesium chloride (10%).[168,169] Fig. 57 shows the polythermal projection obtained from which can be seen the three crystallization surfaces corresponding to $CaCl_2$ + 10%$MgCl_2$, $CaCl_2,KCl$ + 10%$MgCl_2$ and solid solution KCl + NaCl +

10%$MgCl_2$.

TABLE LXXIV.- SOLID PHASES IN THE SYSTEM SODIUM-POTASSIUM-CALCIUM-STRONTIUM-CHLORIDE-WATER

		Composition			
Solid Phases	Temp. °C.	$SrCl_2$	$CaCl_2$	KCl	NaCl
IV + VI + VIII	18	0·5	39·6	2·7	0·3
I + II + VI + VIII	36·5	1·0	50·2	6·7	0·3
III + V + VI + VIII	100	2·5	57·2	3·0	1·0

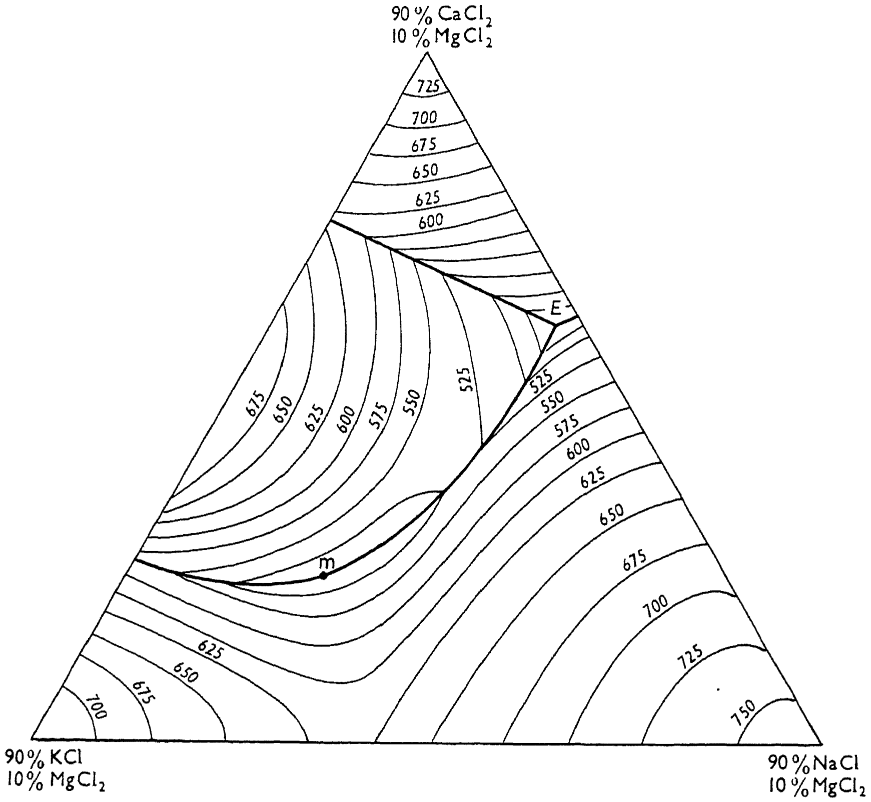


FIG. 57. POLYTHERM FOR THE SYSTEM KCl-NaCl-$CaCl_2$ + 10%$MgCl_2$

At the junction of the fields $CaCl_2$,KCl and KCl+NaCl a minimum *M* is obtained at 495°C. and all three fields meet at 450°C. (Point *E*, Fig. 57) of composition (mole-%) $CaCl_2$ 47, NaCl 38·5, $BaCl_2$ 14·5. Six solid phases are formed at 25°C. in the system $K^+Na^+Ca^{++}Mg^{++}$ || Cl'-H_2O; they are NaCl, KCl, $MgCl_2,6H_2O$ (bischofite), $CaCl_2,6H_2O$, $KCl,MgCl_2,6H_2O$ (carnallite), $CaCl_2,2MgCl_2,12H_2O$ (tachydrite). The principal constituents of sea water and of the Stassfurt salt deposits are the chlorides and sulphates of sodium, potassium, magnesium and calcium which together with water form a six component system. Because of the extreme complexity of the system, only a limited number of isothermal relations have been obtained between 0° and 83°C., and have been used in the interpretation of geological records of salt deposits.[170,171] Investigation has been made of reactions occurring in solid oceanic salts, and the influence of pressures up to 10,000 atm. on these reactions has been considered.[172]

Systems Containing Other Cations.

The influence of hydrogen ions on solubility has been studied in the reciprocal system $2NaCl + H_2SO_4 \rightleftharpoons Na_2SO_4 + 2HCl$ in order to obtain optimum conditions for utilizing the sodium sulphate which accumulates in spinning baths during the manufacture of artificial silk.[173-176] By adding a mixture of nitric acid and hydrochloric acid, the effect of hydrogen ions on the system $NaCl + NaNO_3\text{-}H_2O$ was studied isothermally at 15°, 25° and 35°C.[23] Double decomposition, $RbNO_3 + NaCl \rightleftharpoons NaNO_3 + RbCl$, has been studied by visual observation of onset of crystallization and isotherms constructed at 50°C. intervals below 500°C.[177] Temperatures and compositions of the three eutectic points observed are given in Table LXXV.

TABLE LXXV.- EUTECTIC POINTS IN THE SYSTEM SODIUM CHLORIDE-RUBIDIUM NITRATE

Temp. °C.	Composition of solid mole-%		
156	$NaNO_3$ 36·5	NaCl 5·5	$RbNO_3$ 58
210	NaCl 14	$RbNO_3$ 75·1	$m RbNO_3, n RbCl$ 10·9
330	RbCl 29·5	NaCl 23·6	$m RbNO_3, n RbCl$ 46·9

The stable couple is $RbNO_3 + NaCl$. Rubidium chloride, like potassium chloride, forms a double salt with calcium chloride and m.p. determinations of ternary mixtures $RbCl + NaCl + CaCl_2$ have shown four regions of crystallization, three of which represent pure salts and the fourth the double salt $RbCl,CaCl_2$.[178] Two eutectics exist, one at 500°C. of composition (mole-%) RbCl 2·5, NaCl 45, $CaCl_2$ 52·5; the second at 505°C. with RbCl 56·0, NaCl 32·8, $CaCl_2$ 11·2. Kendall and Sloane reported a compound NaCl,2LiCl which has not been confirmed. The binary system is believed to form a series of mixed crystals having a minimum at 552°C. and 27 mole-% LiCl.[9,179] The binary KCl-LiCl forms a eutectic at 361°C., thus the ternary KCl-NaCl-LiCl comprises two binary subsystems forming solid solutions and one forming a eutectic. This system, which has been investigated by thermal and crystallographic analysis,[180] is thus of the same type as NaCl-NaBr-NaI, KCl-KBr-KI.[15] The system $Na_2SO_4\text{-}Na_2CO_3\text{-}NaCl$ containing a trace of lithium salts has also been investigated.[26] Owing to lowering of the vapour pressure of beryllium chloride by sodium chloride little loss occurs on heating. A eutectic is formed at 215°C. and a break in the solubility curve indicates a compound $2NaCl,BeCl_2$ melting incongruently at 320°C.[181,182] A similar type of compound is formed in the system sodium chloride-aluminium chloride.[183,184,189] This compound $NaAlCl_4$ melts at 152°C.,[184] 155°C.,[183] without decomposition at the limit of congruence,[183] and forms a eutectic at 39[184] or 19[183] mole-% NaCl which melts at 105°C.[183] or 108°C.[184] No evidence has been obtained for the compound $2AlCl_3,3NaCl$ previously reported (Mellor,V,322). The double salt $NaCl,AlCl_3$ has a density of 2·013 and molecular volume 95·32. It boils *in vacuo* at 455°C. and at about 800°C. under 730 mm. of argon, but decomposes rapidly.[183] Vapour pressures above liquid mixtures of sodium and aluminium chlorides have been correlated with the phase diagram and a compound assumed to be $NaCl,AlCl_3$ has been shown to exist in the vapour state above mixtures containing about 50 mole-% of aluminium chloride.[185] Table LXXVI gives temperatures and compositions of eutectics and transitions observed in the ternary system $KCl\text{-}NaCl\text{-}AlCl_3$.[186]

TABLE LXXVI.- EUTECTIC AND TRANSITION POINTS IN THE SYSTEM SODIUM CHLORIDE-POTASSIUM CHLORIDE-ALUMINIUM CHLORIDE

Composition of solid mole-%			Temp. °C.
$AlCl_3$ 66,	NaCl,34,		93 (eutectic)
$AlCl_3$ 71,		KCl 29	114 (eutectic)
$AlCl_3$ 66,	NaCl,20,	KCl 14	70 (eutectic)
$AlCl_3$ 50,	NaCl 50,		146 (transition)
$AlCl_3$ 50,		KCl 50	241 (transition)
$AlCl_3$ 43·5,	NaCl 43·5,	KCl 13	123 (transition)
$AlCl_3$ 54,	NaCl 31,	KCl 15	110 (transition)

Shvartsman[187] obtained a ternary eutectic at 89°C. of composition (mole-%) $AlCl_3$ 63·5, NaCl 20, KCl 16·5. The relevance of this system to the preparation of aluminium by electrolysis is illustrated by the search which has been made for a system homogenous between 670° and 730°C. which would thus be suitable for electrolysis.[188] Aluminium bromide depresses the freezing point of sodium chloride in mixtures containing up to 30 mole-% of sodium chloride. A miscibility gap in the liquid phase begins at very small concentrations of sodium chloride and ends at 7 mole-% NaCl.[190] A review has been published of Russian work done up to 1950 on aluminium halide systems.[191] The system KCl–NaCl–TlCl has a eutectic at 415°C. of composition (mole-%) KCl 6·29, NaCl 6·29, TlCl 87·41, KCl + NaCl solid solution forming above 562–585°C.[43] This work has been extended to a study of $Na^+K^+Tl^+ \| Cl'NO_3'SO_4'$.[76] Nishihara *et al.* studied the system RCl_3–NaCl and RCl_3–NaCl–$CaCl_2$ where R contains either 80%[192] or 89%[193] of cerous chloride, the remainder consisting of other lanthanon chlorides. One eutectic was obtained in each system and its location appears to be independent of whether RCl_3 contains 80% or 89% of cerous chloride. Details of these eutectics are given in Table LXXVII.

TABLE LXXVII.- EUTECTIC POINTS IN THE SYSTEM SODIUM CHLORIDE-CALCIUM CHLORIDE-CEROUS CHLORIDE (RCl_3)

System	Eutectic composition mole-%	Temp. °C.
RCl_3–NaCl	NaCl 54	499
RCl_3–$CaCl_2$–NaCl	RCl_3 21, $CaCl_2$ 48, NaCl 31	459

Using purer material (98% cerous chloride) the ternary system has been investigated by thermal and differential thermal analysis.[194] Nishihara studying RCl_3–NaCl–$BaCl_2$ where RCl_3 contained 89% of cerous chloride, found a ternary eutectic at 373°C. of composition (mole-%) NaCl 42, $BaCl_2$ 22, RCl_3 36.[193,213]

Addition of sodium chloride to silver chloride raises the m.p. continuously, a continuous series of mixed crystals being formed. The feasibility of fractional precipitation in this system, and factors affecting establishment of equilibrium during precipitation, have been studied by Ruff.[195] Because the binaries KCl–NaCl, AgCl–NaCl form continuous series of solid solutions and KCl–AgCl forms a simple eutectic, the ternary system KCl–AgCl–NaCl is of the second type according to Jänecke's classification, no ternary compounds being formed.[43] In the reciprocal system AgBr + NaCl the binaries all form solid solutions, those of NaBr + NaCl and AgBr + AgCl having a minimum and AgBr + NaBr, AgCl + NaCl having neither maximum nor minimum.[15] Considerable similarity has been found between the systems $MgSO_4$–NaCl–H_2O and $FeSO_4$–NaCl–H_2O. Iron astrakanite is similar to magnesium astrakanite in structure and optical properties, and has the formula $FeSO_4,Na_2SO_4,4H_2O$. From this system preparation of very pure $FeCl_3,4H_2O$ is said to be possible.[196] Mixtures of ferric chloride and sodium chloride give a phase diagram having a simple eutectic at 158°C. of composition (mole-%) NaCl 46, $FeCl_3$ 56 and no compound formation has been detected. Measurement of vapour pressures of mixtures of ferric and sodium chlorides enabled the following heat content changes to be evaluated.[197]

Ferric chloride (solid) → Fe_2Cl_6 (gas) ΔH = 33·42 kg.-cal.

Ferric chloride (liquid) → Fe_2Cl_6 (gas) ΔH = 11·27 kg.-cal.

Ferric chloride in liquid of
composition (mole-%) → Fe_2Cl_6 (gas) ΔH = 14·58 kg.-cal.
NaCl 44, $FeCl_3$ 56

The geochemical importance of rinneite ($NaCl,3KCl,FeCl_2$) has led to its study under different conditions. In the quaternary aqueous system it has a small area of stability and dissolves incongruently, as can be seen from the 38° isotherm[9] shown in Fig. 58. At 55°C. this area has been shown to be little affected by Mg^{++}, Ca^{++} or Br'.[198] In order to prevent hydration of zinc chloride, Bergman *et al.*[199] determined m.p. in the system zinc chloride + sodium chloride, in a stream of dry hydrogen chloride. A eutectic is formed at 41·5 mole-% of sodium chloride melting at 262°C. and a compound $ZnCl_2,2NaCl$ melts incongruently at 410°C. Addition of potassium chloride to this produces a ternary system in which three binary compounds are formed between zinc chloride and potassium chloride. The composition and temperature of eutectics, and m.p. of compounds formed in the system $ZnCl_2$-KCl, are given in Table LXXVIII together with details of the three ternary eutectics.

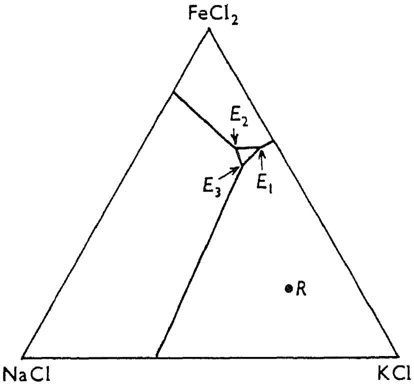


FIG. 58. ISOTHERM AT 38°C. FOR $FeCl_2$-NaCl-KCl SHOWING BETWEEN E_1, E_2 AND E_3 RINNEITE FIELD. R = COMPOSITION OF RINNEITE

TABLE LXXVIII.- CHARACTERISTIC POINTS IN SYSTEMS CONTAINING SODIUM CHLORIDE, POTASSIUM CHLORIDE AND ZINC CHLORIDE

System	Invariant point	Composition (mole-%)	Temp. °C.
KCl + $ZnCl_2$	eutectic	KCl 29	262
	eutectic	KCl 46	228
	eutectic	KCl 68·5	432
	compound	$2ZnCl_2,KCl$	274
	compound	$2ZnCl_2,3KCl$	250 incongruent m.p.
	compound	$ZnCl_2,2KCl$	446
KCl + NaCl + $ZnCl_2$	eutectic	$ZnCl_2$ 60, NaCl 20, KCl 20	203
	eutectic	$ZnCl_2$ 54, NaCl 21, KCl 25	206
	eutectic	$ZnCl_2$ 28·5, NaCl 12·5, KCl 59	402

The system thus resembles that of sodium, potassium and cadmium chlorides (Fig. 59) with the additional compound and eutectic in one subsystem.

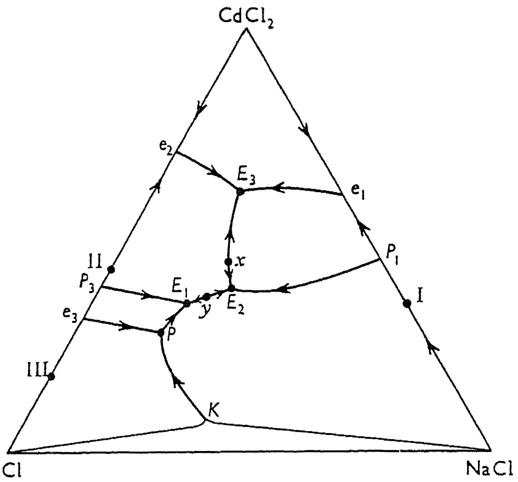


FIG. 59. POLYTHERM FOR THE SYSTEM KCl-NaCl-$CdCl_2$

Aqueous solutions of sodium and zinc chlorides have been shown, by volume change measurements, to form a compound $ZnCl_2$,NaCl at temperatures below 0°C. in addition to $ZnCl_2$,2NaCl also formed in the anhydrous system.[200] Consideration of ionic charges and radii of ions Na^+, Zn^{++} led Bergman *et al.*[201] to suggest the possible existence of a compound $Na^+[ClZnSO_4]'$. The heat of the reaction $2Na_2Cl_2 + ZnSO_4 \rightarrow Na_2SO_4 + ZnCl_2$ was assumed small, thus favouring stability of NaCl + $ZnSO_4$, but thermographic and photomicrographic investigation of binary subsystems and of the reciprocal system failed to produce evidence of such a compound. Five of the ten crystallization fields observed belong to the compounds $ZnCl_2$,2NaCl, $ZnCl_2$,$ZnSO_4$, Na_2SO_4,$ZnSO_4$, Na_2SO_4,3$ZnSO_4$, and a triple compound of unknown composition. The first three compounds are stable over a wide temperature range down to room temperature, but the fourth could not be studied owing to its hygroscopicity and tendency to vitrify. Further investigation[202] has shown that for a given bivalent metal ion e.g. Co^{++}, Mg^{++}, Ca^{++}, the tendency to form compounds of the type $M_1^{++}SO_4,M_2^+X$, where M_1 and M_2 are bivalent metals and X a halogen, is greater for potassium than for sodium or lithium. Hering reported[203] that in the system NaCl-$CdCl_2$-H_2O there existed between 19° and 60°C. two simple salts and three double salts. These are listed in Table LXXIX together with the range of temperature in which they are stable.

TABLE LXXIX.- DOUBLE SALTS OF SODIUM AND CADMIUM CHLORIDES

Double Salt	Temp. °C.
I. $CdCl_2$,2NaCl,3H_2O	stable above 100
II. $CdCl_2$NaCl,H_2O	stable above 37·8
III. 5$CdCl_2$,4NaCl,17H_2O	stable below 43·8

Hering later[204] assigned to II the formula $CdCl_2$,NaCl,2H_2O and to III the formula 4$CdCl_2$,3NaCl,14H_2O in agreement with Bassett.[205] Bassett assigned to I the structure $[Na_2(H_2O)_2]^{II}$ $[Cd_2(H_2O)_2]^{IV}$ Cl_6 to account for the observed formation of solid solutions by replacement of sodium by a bivalent metal ion. Thus sodium as $[Na_2(H_2O)_2]^{II}$ is replaced by $[M(H_2O)_4]^{II}$ where M is Ni^{++}, Co^{++} or Cd^{++}. Of the binary subsystems comprising KCl-NaCl-$CdCl_2$, $CdCl_2$-NaCl forms an incongruently melting compound $CdCl_2$,2NaCl(I) and KCl-$CdCl_2$ forms one compound melting congruently, $CdCl_2$,KCl(II) and one melting incongruently, $CdCl_2,4KCl$(III).[9] A polythermal projection, Fig. 59, shows the compounds and eutectics formed. E_1 E_2 E_3 are ternary and e_1 e_2 e_3 binary eutectics. I II and III denote compounds formed and m is the melting point minimum for solid solutions of sodium and potassium chlorides. Point P is a ternary peritectic (transition) point at which the reaction KCl + liquid $\rightarrow$ $CdCl_2,4KCl$ + NaCl occurs on cooling. P_1 and P_3 are binary peritectics. The critical solution point for NaCl + KCl occurs at about 405°C. (point K Fig. 59) below which the miscibility gap widens rapidly. Temperature maxima x and y are saddle points between the ternary eutectics and arrows indicate the course taken by the liquid composition during crystallization. Like potassium and ammonium chlorides, and unlike chlorides of lithium, caesium and rubidium, sodium chloride forms no double salts with cobalt chloride in water. Isotherms between 25° and 100°C. for the system $CoCl_2$-NaCl-H_2O reveal only the solids NaCl, $CoCl_2,6H_2O$, $CoCl_2,4H_2O$, and $CoCl_2,H_2O$.[206-208] Kendall reported the existence of $2PbCl_2,NaCl$ in aqueous solution at 25°C.[209] but other workers examining the system between 13° and 100°C. were unable to confirm this.[210,211] The equilibrium Ca + 2NaCl $\rightleftharpoons$ $CaCl_2$ + 2Na is increasingly displaced to the right by addition of lead until the ratio Pb/(Ca + Na) is approximately 8 whereupon further addition produces no displacement. Antimony produces displacement in the same direction but to a different degree.[152] The influence of lead on the equilibrium KCl + Na $\rightleftharpoons$ NaCl + K has also been studied.[212] Examination of mixtures containing up to 90% by weight of zirconium chloride in sodium chloride[214] has revealed three eutectics melting at 390°, 220° and 162°C., two compounds, $4NaCl,ZrCl_4$ melting at 535°C. and $NaCl,ZrCl_4$ melting at 330°C. respectively, and a possible third compound $2NaCl,ZrCl_4$. Solubility relations in the system NaCl-$PtCl_4$-H_2O investigated at five temperatures[215] have shown several solid phases to be present at each temperature. Table LXXX gives the solid phases observed and the corresponding temperatures. Solid solutions are represented as enclosed in brackets.

TABLE LXXX.- SOLID PHASES IN THE SYSTEM SODIUM CHLORIDE-PLATINIC CHLORIDE-WATER

Temp. °C.	Solid phases present
40	$PtCl_4,5H_2O$ (I), [I + II], $Na_2PtCl_6,6H_2O$ (II)
60	$PtCl_4,4H_2O$ (III), [III + II]
80	$PtCl_4,3H_2O$ (IV), [IV + II], II, [II + NaCl], NaCl
90	IV, [IV + II], II, NaCl
98	IV, [IV + II], II, [II + NaCl], NaCl

Two modifications of $PtCl_4$ exist in the system, one red and the other yellow. The reciprocal system NaCl + K_2MoO_4 has been shown[216] by visual observation of freezing points to contain three compounds, Na_2MoO_4,K_2MoO_4 (I), $Na_2MoO_4,2K_2MoO_4$ (II), and $NaCl,Na_2MoO_4$ (III). I and II melt incongruently, and III congruently at 644°C. Details of transitions and the eutectic observed are given in Table LXXXI.

TABLE LXXXI.- SOLID PHASES IN THE SYSTEM SODIUM CHLORIDE-POTASSIUM MOLYBDATE-WATER

Composition of solid (mole-%)			Solid phases present	Temp. °C.	Invariant point
NaCl	K_2MoO_4	Na_2MoO_4			
41	53·5	5·5	KCl, K_2MoO_4,II	527	transition
42	47	11	KCl, II, III	507	eutectic
30	35	35	I, II, III	543	transition
19	24	57	Na_2MoO_4, I, III	560	transition
49·5	41·5	9	NaCl, KCl, III	524	transition

Systems Containing Organic Phases.

A compound $(C_6H_{12}O_6)_2,NaCl,H_2O$ is formed at 24°C. in the system sodium chloride–glucose–water. It is decomposed by water and may be reprecipitated by addition of sodium chloride.[217] Existence of a compound $C_{12}H_{22}O_{11},NaCl,2H_2O$ in the system sucrose–sodium chloride–water at 25°C. has been confirmed by vapour pressure and solubility measurements,[218] but no evidence has been obtained for compound formation in the system dextrose–sodium chloride–water at 30°C.[219] Recovery of phenol from dilute aqueous solutions by distillation at atmospheric pressure is difficult owing to formation of an azeotropic mixture containing little phenol, but by adding sodium chloride (producing a deviation from ideality) and distilling at high pressure, recovery is made feasible. Isopiestic equilibrium data at 1 atm. pressure and at 45 lb./sq. in. have been obtained for sodium chloride + phenol + water in the range 0–17% by weight of sodium chloride and phenol concentrations up to saturation, in order to obtain optimum conditions for recovery of phenol.[220] The action of sodium chloride in systems sodium chloride–butyric acid–water and sodium chloride–*iso*butyric acid–water is normal in that its addition renders acid and water less soluble in each other, and raises the critical point.[233] The effect of sodium chloride on the miscibility of *iso*propanol and *tert.*-butanol with water has been studied as part of a wider study of salting-out agents.[221,222] In the system *tert.*-butanol–sodium chloride–water at 30°C. the binodal curve lies near to the water apex of the triangular ternary diagram, and the plait point is of composition (weight-%) 4·6% NaCl in the salt-rich phase, 23% *tert.*-butanol in the alcohol-rich phase.[221] Similar behaviour is exhibited by *iso*propanol.[222] At 25°C. the system *iso*propanol–sodium chloride–water has a plait point of composition (weight-%) 5·2% NaCl in salt-rich phase, 49·5% of *iso*propanol in the alcohol-rich phase. Crystallization of small quantities of material from solution can often be effected by salting-out. This is not always the case, and isolation of antipyrine by salting-out with sodium chloride sometimes results in an apparently metastable liquid phase, particularly when the solution is above room temperature.[223] By turbidimetric study of the influence of sodium and barium chlorides on precipitation of barium sulphate in the systems $BaSO_4$–$BaCl_2$–ethanol–water, and $BaSO_4$–NaCl–ethanol–water, Tananaev *et al.*[224] have shown that a high degree of dispersion of precipitated barium sulphate may be attained either by retarding crystallization *i.e.* by adding a reagent (in this case sodium chloride) which enhances the solubility of barium sulphate, or by accelerating formation of primary particles as compared with the secondary process of aggregation. A barium sulphate precipitate formed in presence of barium chloride or sodium chloride is crystalline, and thus differs from the loose flaky precipitate formed in their absence. These considerations are of considerable importance in analytical chemistry. In soap–water–sodium chloride systems there exist, over limited ranges of temperature and concentration, variable binary and ternary phases. Excluding vapour, five phases commonly occur and these are listed in Table LXXXII.

TABLE LXXXII.- PHASES IN THE SYSTEM SODIUM CHLORIDE-SOAP-WATER

Common name of phase	Description
nigre	an isotropic solution of soap and salt of colloidal nature
middle soap	a single liquid crystal phase of variable composition, viscous
neat soap	similar to middle soap but less viscous
curd	a single crystalline form of solid soap
lye	a liquid containing little soap

The system sodium palmitate–sodium chloride–water has been studied in the range 80° to 290°C.[225] Fig. 60 represents the 90°C. isotherm,[226] lettered regions corresponding to the following phases: *A* curd, *B* curd + neat, *C* neat, *D* neat + middle, *E* middle, *F* middle + nigre, *G* nigre, *H* nigre + lye, *J* neat + nigre + lye, *K* neat + nigre, *L* middle + neat + nigre, *M* neat + lye, *N* neat + curd + lye, *P* curd + lye, *R* curd + lye + sodium chloride, *S* curd + sodium chloride. Table LXXXIII gives some equilibria and the temperature ranges over which they obtain.[225]

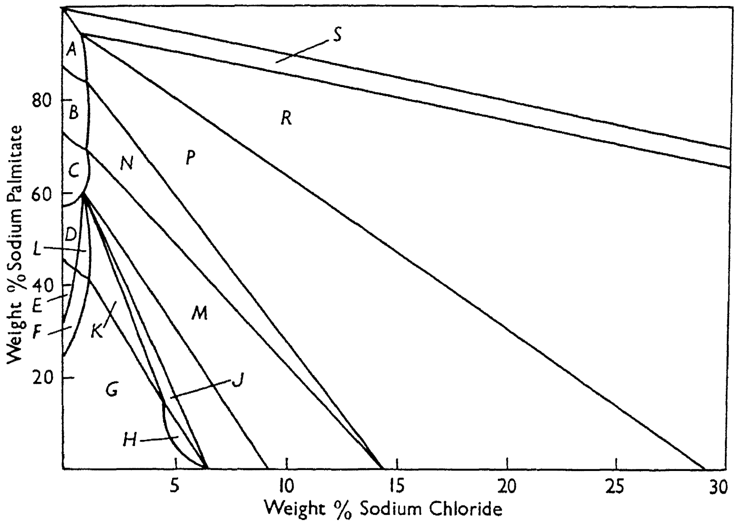


FIG. 60. 90° ISOTHERM FOR THE SYSTEM SODIUM PALMITATE-SODIUM CHLORIDE-WATER

TABLE LXXXIII.- EFFECT OF TEMPERATURE ON THE PHASES PRESENT IN THE SYSTEM SODIUM CHLORIDE-SOAP-WATER

Phases present	Temp. °C.
curd + neat + middle + lye + vapour	80.8
neat + nigre + lye + vapour	81 to 290
neat + middle + nigre + vapour	81 to 152
curd + neat + lye + vapour	82 to 112

Non-separation of phases in this system at high temperatures leads to difficulty in analysis of phases and observation of phase changes and an iso-piestic vapour pressure method has been evolved and applied to a study of the system at 90°C.[226] Fig. 60 shows the isotherm thus obtained. The system sodium laurate-water-sodium chloride has been studied in the range 25° to 310°C. by three methods:[227] (*a*) observation of the temperature at which phase changes occur in systems of known composition, (*b*) examination of a limit by preparation of two systems of closely similar composition, so that the limit lies between them, (*c*) analysis of separated phases. The methods agree quantitatively, thus enabling areas within the system to be discerned. Phase relations in the system sodium laurate-sodium palmitate-sodium chloride-water have been obtained at 90°C.[228] The phase boundaries lie intermediate between those for the single soap systems but nearer to those of the sodium laurate system than would be expected if the salting-out effect were additive.

Vapour pressure measurements have shown Kettle wax to be an important phase in soap–water–electrolyte systems.[229] Other soap systems[230] and those containing modified soaps of the type Na(C_8–C_{18}) alkyl sulphate, the alkyl and alkylarene sulphonates[231] have been studied. McBain *et al.*[227,229,232] have considered the applicability of the phase rule to soap–electrolyte–water systems and consider that it describes the behaviour of such systems adequately.

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THE CHEMICAL PROPERTIES AND USES OF SODIUM CHLORIDE

By J. M. THOMAS

This sub-section falls into six main parts. First, a brief descriptive account is given of the chemical reactions of the salt which were either unknown or incompletely understood when the original Treatise was published:

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this part includes an account of the corrosion of metals and alloys by sodium chloride. Secondly, a summary of the available thermodynamic data relating to some of these reactions is presented. Thirdly, chemical reactions which are influenced by the presence of trace amounts of sodium chloride are discussed. Fourthly, adsorption phenomena involving the salt both as adsorbent and adsorbate are considered. Fifthly, available data on the physiological and biochemical importance of sodium chloride is briefly discussed. And finally an outline of the laboratory and industrial uses of the salt is given.

Chemical Reactions

Thermal decomposition of sodium chloride can occur at quite low temperatures depending on the nature of the supporting material. Noticeable decomposition begins on molybdenum at 300°C., and on tungsten at 400°C., whilst on zinc and cadmium decomposition does not commence below 675°C.[1] When metallic copper is plunged into molten sodium chloride, atoms of both copper and sodium in their elemental forms appear in the vapour phase, the latter being in much greater preponderance.[2] In a sealed tube at 100°C., sodium chloride reacts slightly with dinitrogen tetroxide, N_2O_4, to form nitrosyl chloride, NOCl.[3] In a coal gas-air flame, the chlorine is completely removed from the sodium chloride as hydrogen chloride.[4] And in a dry sulphur dioxide-oxygen mixture at high temperature a series of reactions occur most of which produce sodium sulphate:[5]

$$2NaCl + 2SO_2 \rightleftharpoons Na_2SO_4 + Cl_2 + S$$

$$2NaCl + SO_2 + O_2 \rightleftharpoons Na_2SO_4 + Cl_2$$

$$Na_2SO_4 + 3NaCl \rightleftharpoons Na_2SO_4.3NaCl$$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$$3SO_2 \rightleftharpoons 2SO_3 + S$$

$$2S + Cl_2 \rightleftharpoons S_2Cl_2$$

Sodium sulphate may also be produced from sodium chloride metathetically. With zinc sulphate a double salt, $2NaCl,ZnCl_2$, is formed[6] along with the sodium sulphate, and formation of the latter ceases as soon as free sodium chloride is no longer present. With magnesium sulphate, conversion into sulphate occurs smoothly at temperatures in the range 750°–800°C.; a higher temperature leads to volatilization of the sodium chloride.[7,8] When the sodium chloride-sodium sulphate mixtures produced by metathesis are suspended in water and treated with ammonia and then saturated with carbon dioxide at 35°C., sodium bicarbonate is produced, 75% of the sodium being converted in 3-4 hr.[9,10]

Sodium chloride may be converted efficiently to sodium sulphate by means of the Hargreaves reaction according to the following equation:

$$2NaCl(s) + SO_2(g) + \tfrac{1}{2}O_2(g) + H_2O(g) \rightleftharpoons Na_2SO_4(s) + 2HCl(g)$$

In the presence of any catalyst of spinel-like structure, and especially in the presence of magnesium aluminate, $MgAl_2O_4$, the optimum temperature for producing sodium sulphate lies in the temperature range 600°–635°C.[11]

Conversion of sodium chloride to sodium nitrate may be effected by passing an air stream loaded with nitric acid and water vapour over the polycrystalline salt at 130°C., the conversion:

$$3NaCl(s) + 4HNO_3(g) \rightleftharpoons 3NaNO_3(s) + NOCl + 2H_2O(g)$$

being catalyzed by moisture.[12,13] The rate of this reaction decreases markedly with increasing temperature.[12]

The reaction described by Mellor (II,553) whereby sodium hydroxide is generated from sodium chloride by water vapour at elevated temperatures has been frequently used[14-18] to extract phosphorus in useful form from various rock phosphates. It is believed[14] that the sodium hydroxide, produced above 700°C. by the reaction of sodium chloride with water vapour, reacts in turn with aluminium phosphate, $AlPO_4$, and other phosphates to produce complexes of the phosphates of sodium, aluminium and calcium. An equimolecular mixture of sodium metaphosphate and sodium chloride, heated to 650°–750°C. in the presence of air, reacts[19] according to the equation:

$$2NaCl + Na_2P_2O_6 + \tfrac{1}{2}O_2 \rightleftharpoons Na_4P_2O_7 + Cl_2.$$

Below 400°C., sodium chloride acts merely as a catalyst in the polymerization or the isomerization of the metaphosphate.[19]

Sodium chloride forms a solid solution with sodium hydroxide when a mixture of the compounds is heated above 800°C.[20] Fusion of sodium chloride with mirabilite, $Na_2SO_4,10H_2O$, at 50°–75°C. invariably results in the formation of a film of tenardite, anhydrous sodium sulphate, on the crystals of sodium chloride whether the latter are large or small.[21]

With aluminium oxide in the presence of moist air and at temperatures between 830° and 1050°C., sodium chloride forms sodium aluminate and gaseous chlorine according to the reaction:[22]

$$4xNaCl + yAl_2O_3 + xO_2 \rightleftharpoons 2xNa_2O,yAl_2O_3 + 2xCl_2.$$

But this reaction is subsidiary to another,

$$2xNaCl + yAl_2O_3 + xH_2O \rightleftharpoons xNa_2O,yAl_2O_3 + 2xHCl,$$

and the gaseous hydrogen chloride so produced is oxidized to gaseous chlorine by the oxygen of the air.[22] For the complete reaction of sodium chloride with aluminium oxide in this manner it appears[22] that an excess of the oxide is of greater importance than an excess of moisture.

Silica reacts with sodium chloride in a way very similar to the alumina-sodium chloride reaction just described.[23]

$$4xNaCl + ySiO_2 + xO_2 \rightleftharpoons 2xNa_2O,ySiO_2 + 2xCl_2,$$
$$2xNaCl + ySiO_2 + xH_2O \rightleftharpoons xNa_2O,ySiO_2 + 2xHCl$$

and

$$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2.$$

And, as with alumina, all three reactions proceed in moist air but the second predominates.[23] Here, however, the reactions begin at about 600°C., increase gradually up to 1000°C. and then become markedly greater at slightly higher temperatures.[23] In dry nitrogen no reaction occurs, but in the moist gas at 1000°C. 18·7% of the sodium chloride is converted to hydrogen chloride after 36 hr.[23] At a fixed temperature quartz participates in the reaction more readily than tridymite or silica freshly precipitated by neutralizing sodium silicate.[23] Unlike the alumina–sodium chloride reaction, the ratio of silica to sodium chloride is of secondary importance; the important factor here is the amount of surface area exposed to the gas.[23] The three reactions quoted above, together with the following

$$NaCl + NaHSO_4 + SiO_2 \rightleftharpoons Na_2SiO_3 + SO_3 + HCl$$

which occurs[24] in the temperature range 150° to 1300°C., and the interaction of sodium chloride and kaolin at 900° to 1000°C.[25] are of great importance in the manufacture of sodium silicate and in the glass industry generally.

The reaction between molybdenum trioxide and sodium chloride in the presence of air and inert gas proceeds at 400° to 700°C. with the formation of the oxychloride and molybdate, MoO_2Cl_2 and Na_2MoO_4 respectively; in the presence of air only, chlorine gas is evolved.[26]

Sodium chloride and aluminium trichloride readily form a fusion mixture which is suitable as a medium for the study of other chemical reactions e.g. intramolecular cyclizations, Fries rearrangements, and the condensation of p-hydroxyphenol with various mono- and di- basic acids in such a melt at 180° to 200°C. have been studied.[27] Theoretical evidence shows[28,29] that the four-co-ordinated (tetrahedral) complex ion, $NaAlCl_4$, is stable under these conditions.

Corrosion by Sodium Chloride

From general electrochemical considerations solutions of sodium chloride can be expected to promote the corrosion of metals and alloys. In the first place, the coherent superficial oxide films which protect most of these materials are known[30] to be pervious to chloride ions, and it is for this reason that many metals, particularly iron,[31] tend continuously to dissolve in chloride solutions. Secondly, whenever dissimilar metals or alloys, or even sections of the same material in different energetic conditions (due to slightly different pretreatments, etc.), are in juxtaposition, there is always the tendency for the less noble component to dissolve if a short-circuited voltaic cell can be set up. The rate at which dissolution of the anodic component of this voltaic cell occurs, *i.e.* the rate of corrosion, is governed by Faraday's Laws and hence is the greater the larger is the current flowing in the cell. It is clear therefore that, if a solution such as sodium chloride, which has a high electrolytic conductance, separates one metal from another, less noble metal, dissolution of the latter will be enhanced.

The corrosion by aqueous sodium chloride solutions of virtually all the metals and very many alloys has been studied both empirically and from a fundamental viewpoint for over 50 years. One general review of this field, dealing in particular with corrosion of constructional materials including iron, stainless steel, mild steel, nickel, lead, tantalum, aluminium and alloys based on these metals has been published[32] in the U.S.A. Another equally comprehensive review including tables of corrosion resistance of commonly used structural materials to attack by sodium chloride solutions, has recently been published[33] in the U.S.S.R. Other less exhaustive accounts[34-37] and a bibliography[38] of corrosion of structural materials - mainly those used in boilers, pipes and oil-wells - are available.

Details of the mechanisms and rates of corrosion of various substances are considered in sections of this Treatise devoted to the substances undergoing corrosion. Only an outline of some of the practical aspects of metallic corrosion by sodium chloride, and methods of converting it, are given here.

The presence of free oxygen appears to be necessary for the corrosion of copper by aqueous sodium chloride[39] and by sea water.[40] The presence of oxygen, as well as intermittent access of sodium chloride solution to various parts of the metal surface, also favours the corrosion of aluminium.[41] Intermittent access of salt solution to the surface of duralumin,[42] or duralumin clåd with aluminium,[43,44] again causes severe metallic corrosion. Apparently the comparatively facile corrosion of duralumin alloys is associated with the presence of copper.[42-45] There is reason to believe that some of the alloy is first dissolved by the sodium chloride solution and the copper is then reprecipitated. In the regions where the copper has been deposited hydrogen overvoltage is reduced so that hydrogen liberation and therefore localized corrosion is enhanced.[45] The attack on electrolytic zinc by sodium chloride solution is greater than by sea water because the magnesium salts in the

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latter develop a protective film on the metal surface.[46] Steel containing 0·18% of carbon shows less difference between the effects of sea water and salt solution than does zinc, but the total corrosion is greater.[46] The rate of penetration of a 0·5 N. sodium chloride solution into a mild steel specimen which, while totally immersed, is rotated at a speed of 260 r.p.m. is 7·0 mm. per year: with increasing rotation rates the rate of corrosion decreases.[47] The rate of corrosion by a 0·1 N. sodium chloride solution in the temperature range 22° to 30°C. of a mild steel specimen which has been grit-blasted is greater than that of a similar specimen which has been mechanically cleaned with emery.[48]

The corrosion of a lead–silver alloy and of graphite - materials used as electrodes in the large scale electrolysis of sodium chloride solutions - have also been studied.[49,50]

There are three main methods of combating the corrosion of constructional materials by sodium chloride solutions:- cathodic protection, suitable alloying, and the use of inhibitors. The first of these, which is now being used increasingly, consists in applying an electric potential between an inert anode, usually carbon, with the metal to be protected serving as the cathode, so that a small continuous current flows; e.g. a duralumin plate 1 mm. thick immersed in 3% sodium chloride at 40°C. when rendered cathodic shows a maximum resistance to corrosion when the cathode current density is 2–6 m. amp. $\mathrm{cm.}^{-2}$.[51,52] In the second method, resistance to corrosion is increased by the incorporation of a small quantity of foreign metal on to or into the surface of the metal or alloy to be protected, e.g. for both iron and a 0·47% carbon steel saturation of the surface with vanadium[53] or manganese[54] is effective. Corrosion inhibitors, which are either inorganic salts such as alkali metal dichromates,[55,56] phosphates,[55,56] or nitrites,[57] or organic substances such as thiourea[58] or alkali metal benzoates[59] are thought to function through reacting chemically with the metal surface and forming an impermeable layer of the corresponding metal salt or salts, e.g. the presence of monosodium dihydrogen phosphate in a sodium chloride solution prevents corrosion of steel since a thin protective layer of ferric phosphate, $Fe_3(PO_4)_2$, is formed.[60]

The practice of using sodium chloride to thaw ice and snow on busy highways has caused concern amongst motorists since it leads to increased corrosion of the bodies of motor vehicles. Indeed, in Rochester, N.Y., some polyphosphate–nitrite corrosion inhibitor was added to the salt used for that purpose.[61-63]

Thermodynamics of Reactions Involving Sodium Chloride

Relatively few direct determinations of the thermodynamics of these reactions have been made. Attention has been focused mainly on the measurement of equilibrium constants at a few temperatures.

In the reaction:

$$\mathrm{NaCl + H_2O \rightleftharpoons NaOH + HCl}$$

the equilibrium pressure product, $p_{\mathrm{NaOH}} \cdot p_{\mathrm{HCl}}$, is approximately $1{\cdot}6 \times 10^{-7}$ $\mathrm{atm.}^2$ at 750°C.[64] At 825°C. the concentration product $[\mathrm{Na}]^3[\mathrm{Al^{III}}]$ relating to the system:

$$\mathrm{3NaCl + Al \rightleftharpoons 3Na + AlCl_3}$$

is $5{\cdot}2 \times 10^{-10}$, whilst at 900°C. it is $5{\cdot}8 \times 10^{-10}$.[65]

For melts of sodium chloride and aluminium trichloride, the vapour pressures of the trichloride have been determined from 150°C. to 560°C.[66] and at 700°C.[67] The values of the constants A and B in the equation:

$$\log p = -\left(\frac{A}{T}\right) + B \ldots\ldots\ldots (1)$$

where p is the vapour pressure of the aluminium trichloride at a temperature T°K., are shown in Table LXXXIV.[66]

TABLE LXXXIV.- VAPOUR PRESSURE OF SODIUM CHLORIDE-ALUMINIUM TRICHLORIDE MELTS (150–560°C.)

% $AlCl_3$	Constants in Equation[1]	
	A	B
65·5	2004·0	6·321
59·4	2284·0	5·416
51·8	4673·0	7·181

The heats of formation of the ammoniate of sodium chloride, $NaCl,5NH_3$, from solid salt and gaseous ammonia and from solid salt and liquid ammonia, at various temperatures have been measured.[68] The decomposition pressure, p, of the ammoniate is given by:[68]

$$\log p = -\left(\frac{1781{\cdot}90}{T}\right) + 10{\cdot}08979 \dots\dots\dots (2)$$

where T is the absolute temperature.

The equilibrium pressure of hydrogen chloride produced by the reaction:

$$NaCl(s) + NaHSO_4(s) \rightleftharpoons Na_2SO_4(s) + HCl(g)$$

varies with pressure according to the equation[69]

$$\log p_{(mm)} = -\left(\frac{2241{\cdot}2}{T}\right) - 8{\cdot}2510 \dots\dots\dots (3)$$

Under the standard thermodynamic condition of 1 atm. pressure of hydrogen chloride, and at temperatures less than 100°C., the Gibbs free energy change of the above reaction is given by:[69]

$$\Delta G^0 = 12057 + 5{\cdot}4 \times 2{\cdot}203.T.\log T - 61{\cdot}4.T \text{ g.-cal. mole}^{-1},$$

where T is the temperature in degrees Kelvin. Under the same conditions, the enthalpy change is:[69]

$$\Delta H^0 = 12057 - 5{\cdot}4T \text{ g.-cal. mole}^{-1}$$

For this reaction also the growth of hydrogen chloride gas pressure is logarithmic with respect to time.[69]

The endothermicity of the reaction:

$$2NaCl(s) + H_2O(g) + SiO_2(g) \rightleftharpoons Na_2SiO_3(s) + 2HCl(g)$$

is about 70 kg.-cal.[70] and the optimum conditions for this reaction, which is of considerable importance in the manufacture of glass using sodium chloride, have been evaluated.[70]

Thermodynamic studies have been carried out on the fluorine-chlorine exchange in the sodium chloride-sodium fluoride system,[71] the reaction of sulphur trioxide gas with sodium chloride,[72] the interaction of sulphur and sodium chloride in the presence of oxygen,[73] and the metathesis:

$$Ca(CN)_2 + 2NaCl \rightleftharpoons CaCl_2 + 2NaCN$$

from 480° to 1520°C.[74]

Reactions Catalyzed by Sodium Chloride

In recent years many reactions have been investigated in the presence of traces of sodium chloride. These are predominantly oxidations and reductions.

Like most other alkali metal halides, sodium chloride, when deposited on the inner walls of the containing vessels, affects the kinetics of gas-phase reactions of hydrocarbons and hydrogen with oxidizing gases.[75,76] The inhibition of the combustion of hydrogen when carried out in a sodium chloride coated vessel has been attributed to the recombination of hydrogen atoms and hydroxyl radicals on the salt surface.[75] It seems[75] that for a series of alkali metal halides, the lower is the lattice energy, the greater is the catalytic activity. The oxidation of carbon monoxide by nitrous oxide is also catalyzed by sodium chloride, and, in this instance, sodium atoms are believed to act as intermediates.[77] Another oxidation catalyzed by sodium chloride in which sodium atoms have been postulated as intermediates is the gasification of carbon.[78-81] The gasification of most of the many forms of carbon with solids such as potassium chlorate and with oxidizing gases such as oxygen, carbon dioxide, water vapour and nitrous oxide is catalyzed by alkali salts in general whether the latter are present originally as impurities or are added by impregnation.[82-84] Besides catalyzing the gasification of carbon in its several forms sodium chloride also catalyzes the carbonization of coal: the marked change in the composition of this product in the catalyzed carbonization process as compared with the normal process is probably due to the inhibition by sodium chloride of the cracking of the hydrocarbons formed.[85]

The explosion of molten ammonium nitrate mixed with a powdered metal is greatly accelerated when sodium chloride is present.[86-88] It has also been observed that the initiation of certain explosions can be affected by the presence of rock salt grit.[89]

In the catalytic decomposition of hydrogen peroxide solution by sodium chloride, potassium chloride or barium chloride, a new kind of salt effect in chemical kinetics has been observed.[90,91] If γ is the ratio of the velocities of reaction with and without salt, and c is the salt concentration in mol. l^{-1} then, at low values of c,

$$\frac{1}{\gamma} = 1 - \sigma c$$

where σ is a constant and equal to 0·5 for sodium chloride (σ = 1·0 and 1·4 for potassium chloride and barium chloride respectively).[91] This effect can be explained by assuming that hydrogen peroxide is 'salted out' from the vicinity of the catalyst ions, and therefore is in increased concentration in the remainder of the solution. And since the decomposition of hydrogen peroxide is a bimolecular reaction, the increase of the peroxide concentration leads to an increase in the rate of reaction. It has been calculated[91] that the 'effective' concentration of a nominally 5 M. hydrogen peroxide solution in the presence of 2·5 N. sodium chloride is 25 M.

One interesting physical reaction which is catalyzed by sodium chloride is the allotropic conversion of quartz to cristobalite at high temperatures. This effect was discovered[92-94] during attempts to prepare ceramic materials, for use as roof tiles, free from efflorescent sulphates. A typical ceramic of this type is made by heating mixtures of silica (quartz, tridymite or cristobalite) and calcium sulphate at about 1000°C. with sodium chloride as a mineralizing agent.[93]

At high pressures (4770kg. cm.$^{-2}$) and at ordinary temperatures, urea may be synthesized from ammonium carbonate by either isothermal or adiabatic compression.[95] Yields are doubled, however, in the presence of sodium chloride.[95] Salt is also effective in increasing the yield of sodium cyanide synthesized from sodium carbonate, carbon, ferric oxide and atmospheric nitrogen.[96]

Interest has recently been centred on the part played by various crystalline halides, notably silver iodide and sodium chloride, in the freezing of water droplets.[97–99] The salts act as nuclei for the condensation of water vapour and its subsequent solidification, factors relevant to the artificial production of rain.

Other reactions catalyzed by sodium chloride include the oxidation of sulphur, by bromine when the sulphur is suspended in water[100] or by air when it is present in coal,[101] the oxidation of thiosulphate ions,[102] iodide ions[103] and iodine,[103] the conversion of dolomite to magnesium sulphate by strong sulphuric acid,[104], the parahydrogen conversion[104 a,b] and the thermal decomposition of sodium cyanamide, Na_2CN_2.[105] The reduction of chromite, $FeCr_2O_4$, by hydrogen or graphite[106] and the reduction of alkaline permanganate[107] are also catalyzed by sodium chloride.

A reaction which is retarded by sodium chloride is the mutarotation of dextrose in water, the retardation increasing with the concentration of salt.[108] On the other hand, the addition of sodium chloride to dextrose in hydrochloric acid solution increases the rate of mutarotation.[109,110] All the following sugars undergo mutarotation at a slower rate in water in the presence of sodium chloride:[111] *α–D*–glucose, *α–D*–galactose, *α–D*–xylose, *β–L*–arabinose, *α*–lactose and *β*–maltose. Not only is the rate of mutarotation influenced, but the absolute magnitudes of the optical rotation of sugars and tartaric acids are also affected by sodium chloride.[112,113] Britton and Jackson[113] suggested that the reduction in the molar rotation of tartaric acid is due to the hydration of the sodium and chloride ions.

The results of several investigators on the influence of sodium chloride in the inversion of sucrose have been critically assessed.[114]

Adsorptions Involving Sodium Chloride

Much more is now known about adsorption processes in which sodium chloride acts as adsorbent than about those in which it acts as adsorbate. Attention has been chiefly directed to the study of adsorption of gases on the crystalline salt.

Early work dealt with the rates and heats of adsorption, at both low and high temperatures, of the following gases: water vapour,[115,116] nitrogen,[116] hydrogen,[116] carbon dioxide,[116] nitrogen dioxide,[116] methane,[116] ethane,[116] propane,[116] nitrous oxide,[116] sulphur dioxide,[116,117] ammonia[117] and methanol vapour.[118] Subsequently Tompkins[119] carried out a comprehensive adsorptive study at low pressures and low temperatures (–78·2°, –183° and –192°C.) on a sodium chloride sample the surface area of which had been estimated microscopically to be 45000 cm.^{2}. Although this figure may not have been the true physical area of the sample, no reliable method of estimating surface areas being then available,[120] this work marked the commencement of accurate quantitative studies of physical adsorption and chemisorption on sodium chloride. The gases used by Tompkins were:[119,121] argon, carbon monoxide, methane, oxygen, nitrogen, nitric oxide, nitrous oxide, carbon dioxide, cyanogen, ethylene and ammonia. It was found[119,121] that (i) polar gases such as nitric oxide and carbon monoxide are adsorbed extensively, whereas methane is adsorbed only to a small extent; (ii) the heats of adsorption at –183°C. of argon, methane and carbon monoxide are 0·0, 300 and 350 g.-cal. mole^{-1} respectively; (iii) the adsorption of argon at –183°C. diminishes if preceded by a determination of a carbon monoxide isotherm; and (iv) a slow process obeying the laws of diffusion and associated with a heat of activation of 6 kg.-cal. mole^{-1} accompanies the instantaneous reversible adsorption of ammonia.

In recent years, physical adsorption studies on sodium chloride have been pursued for the purpose of testing various theories as to the origins of surface heterogeneity and phase transitions which accompany two-dimensional condensation at low temperatures.[122] Ross and others[122-126] have confirmed the

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existence of a discontinuity in the ethane adsorption isotherms at 122·9°, 131·3° and 136·0°K., and have interpreted the effect as being due to a first-order phase transition in the adsorbed film. The two-dimensional critical temperature of ethane on the (100) surface plane is 132°K.[124] Xenon, methane and diborane exhibit similar characteristics on being physically adsorbed at low temperatures; the observed two-dimensional critical temperatures, again on the (100) surface planes, for these gases are, respectively, 104°, 90° and approximately 133°K.[124]

The adsorption of sodium chloride from aqueous solution by several varieties of charcoal,[127,128] sand,[129] gelatin,[130] silica[131] and many different types[132-142] of commercially available synthetic resins and natural exchangers[143,144] (e.g. starch) has been studied.

Physiological and Biochemical Significance of Sodium Chloride

In the original Treatise attention was directed to the importance of sodium chloride for the proper performance of the physiological functions of the human body. In the intervening years our knowledge in this field has been considerably enlarged.(See also Sect. XLI). This has been due in large measure to the the attention paid to: the role of sodium chloride in regulating acid-base equilibria in blood;[145,146] the optimum salt concentration required for the complete action of immune agglutinins;[147,148] the general significance of sodium chloride in serological reactions,[149-151] the ingestion,[152,153] excretion[154-157] and secretion[158,159] of sodium chloride into and from the body; the effect of depleting the concentration of sodium chloride on the functioning of the central nervous system;[160-161] the influence of salt concentration on the assimilation of glucose;[162] and the vasodilator action of sodium chloride.[163]

As evidenced by its large annual consumption in the applied chemical industry, sodium chloride plays an important part in many processes of biochemical interest. Its effects in the preservation of butter,[164-169] fish,[170-172] fruits,[173,174] hay,[175] eggs,[176] pork[177,178] and other foodstuffs[172,179] have been extensively studied. A fluid found in an Egyptian tomb, consisting of a 3% aqueous sodium chloride solution containing some sodium sulphate as impurity, was used in ancient times as a preservative agent for the internal organs of the dead.[180]

Other fields of interest to the biochemist and botanist where the important effects of sodium chloride have been studied closely, include the salting of cheese,[181-185] the curing of animal skins,[186-189] the curing of timber,[190,191] the swelling of hide powder and chrome tanning,[192-195] the dyeing and finishing of silk[196,197] and wool,[198,199] the improvement of flour,[200,201] the eradication of weeds[202-204] and plant nutrition.[205-209]

The Uses of Sodium Chloride

The extensive use of sodium chloride in general laboratory practice is not the consequence of any specific chemical property of the salt itself e.g. in polarography, where it is used as a supporting electrolyte, in the coagulation and flocculation of sols, in the charging or regeneration of ion-exchange columns, in the preparation of solutions of fixed ionic strength, and in the construction of infra-red lenses[210] or Geiger-Müller counters:[211] other salts, notably other alkali metal halides, could be used and are being used with equal facility. Rock salt components may soon play a significant part in vacuum practice now that a method of attaching the salt to glass or metal tubes has been discovered.[212] Such a joint, which is made by means of a silver-silver chloride graded seal, holds vacuum well.[212]

Both sodium chloride and rock salt, used as solid, aqueous solution or mixed with other materials, find many applications in the chemical industry, of which some examples have been given above. Glass manufacture from silica using sodium chloride as well as or instead of soda is a process which consumes large quantities of the salt annually.[213-224] The addition of sodium chloride in calcining limestone[225-229] is quite common, the process being thereby accelerated.[226] In the production of mortar,[230] concrete[231] and cement[232,233] small quantities of sodium chloride play an important part in the ultimate settling and in the subsequent performance of these materials. The function of the salt in this respect is similar to its role as a stabilizer of highway constructional materials.[234-240] Sodium chloride is used also as a soil stabilizer,[241] as a flux in blast-furnace smelting[242] and as a component of certain explosives.[243]

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SECTION XXXII

SODIUM BROMIDE

By F. CALL

Production and Preparation

The manufacture of sodium bromide through the intermediary of Fe_3Br_8 (Mellor,II,578) still remains the most important method[1-4] although interest is maintained in the reaction of bromine with caustic soda using a variety of reducing agents such as manganese carbonate or hydroxide,[5] urea, cyanamide, etc.,[6] ammonia[7] or formate[8] to prevent the formation of hypobromite.

Sodium bromide 99·5% pure has been prepared by hydrolyzing methyl bromide with methanolic sodium hydroxide at temperatures below 50°.[9] Commercial material may be purified by precipitating sulphate as the barium salt, oxidizing iron by hydrogen peroxide, and precipitating alkaline earths as carbonates. Aluminium, magnesium and silicon are precipitated after adjusting the pH to 6·5 by means of hydrobromic acid and the pure salt is crystallized at pH 1.[10] Crystals of anhydrous sodium bromide are obtained by crystallizing the solution at temperatures above the dihydrate transition point.[11] Large homogeneous crystals suitable for optical, photoelectric or dielectric measurements may be prepared from molten sodium bromide. The temperature must be kept very constant and heat transfer must take place only through a cooling plunger immersed in the melt.[12]

The U.S. permissible limits for barium in sodium bromide are 25 parts in 100,000.[13] Phosphate and sulphate have been found in commercial material.[14]

The hot springs at Mondorf-Etat in Luxemburg have been found to contain 0·1335 g. per l. of sodium bromide.[15]

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Physical Properties

Sodium bromide crystallizes in the cubic system, the length of the unit cell being 5·95 ± 0·01A.[1] More precise determinations with crystals larger than 150A. gave by an electron diffraction method 5·962 ± 0·002A. and by an X-ray method 5·960 ± 0·001A. The dimensions of the unit cell were found to vary with the size of the crystal and the values obtained fell on a smooth curve.[2]

TABLE I. - VARIATION OF UNIT CELL DIMENSIONS
WITH CRYSTAL SIZE FOR SODIUM BROMIDE

Crystal size A.	35	45	50	60	150
a A.	5·913	5·927	5·932	5·947	5·962

It is believed that this is not due to surface contamination.

Data for the standard X-ray diffraction powder pattern are available for reference.[3] Photographs of the dehydration figures for the dihydrate have been published but their interpretation is still not clear.[4]

The density of crystalline sodium bromide has been found to be 3·213 ± 0·003, that of $NaBr,2H_2O$ 2·1655 ± 0·0003; the respective molecular volumes are 32·07 and 64·176.[5] The Brinell hardness is 9·2 and the plasticity coefficient b is 0·0052.[6]

The melting point is quoted variously as 747°C.[7] and 740°C.;[8,9] the boiling point as 1393°C.[9] Vapour pressures above the melting point[9,10,12] are found to fit the equation:-

$$\log p_{\text{atm.}} = \frac{-37000}{4\cdot57\,T} + 5\cdot130$$

Vapour pressures of the solid measured by means of an effusion method are:-[11]

T°K.	891·0	901·5	910·8	914·1	917·4	930·1
$P_{\text{mm}} \times 10^3$	7·65	11·8	15·1	17·5	19·5	35·6

From these vapour pressure data the following heats in kg.-cal.mol.$^{-1}$ have been calculated: of melting 6, of vaporization 36, of sublimation 42, of formation of solid 91.[9] The entropies (g.-cal.°C.$^{-1}$) were found to be S (crystal) 35·1, S (vapour) 67·5 ± 0·5, ΔS (vapour) 32·4, $T\Delta S$ 29·2 ± 1·5 while ΔH (crystal) was 52·4 ± 3·0, ΔH (vapour) 49·6 ± 2·0 kg.-cal.[12]

The foregoing values were obtained by using an assumed value for the heat of fusion of 6·9 kg.-cal. as against the value of 6 calculated above.[9] Earlier values of the entropy are S (crystal) 33·3 and S (vapour) 66·6.[13] The heat of sublimation calculated from the space lattice energy is 55 kg.-cal.,[14] which may be compared with the figure calculated above from vapour pressure data. The heat of dissociation of the vapour measured by an optical method is 82·6 ± 1·5 kg.-cal. as compared with 90·5 kg.-cal. obtained by a thermal method.[15] The free energy and heat content calculated from e.m.f. measurements of a non-aqueous cell are for the reaction:-[16]

$$Na + \tfrac{1}{2}Br_2(l) = NaBr(s)$$

ΔF_{298} – 83·11kg.-cal., ΔH_{298} – 86·24kg.-cal., respectively. The lattice energy has been calculated as 169 at 298°K., 173 at abs.zero,[17] and[13] 174·6 and 171·7 kg.-cal./mol.$^{-1}$.[18]

The relative partial molal heat content of sodium bromide in aqueous solutions has been determined by both e.m.f.[19] and calorimetric measurements[20,21] with only fair agreement. The heat content has a maximum of 38·9 g.-cal.g.$^{-1}$ in 5·5 molal solution.[21] The apparent molal heat content over the ranges 0–2·5M. at 25°C. is expressed by the equation:-

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$$\Phi_c = \Phi_c^0 + Am^{1/2}$$

where Φ_c^0, the value at infinite dilution, is $-24{\cdot}3$ g.-cal.mol.$^{-1}$ and A is 13·6.[22] The partial molal heat capacity C_p g.-cal.g.$^{-1}$ solution is given by $C_p = \Phi_0^c + \frac{3}{2}Am^{1/2}$ and the heat capacity of a given solution by $C_p = (1000 + m\Phi_c)/(1000 + 101{\cdot}9m)$ g.-cal.g.$^{-1}$ solution where m is the molality.[22] The variation of the partial molal heat with temperature can be expressed at any concentration by $L = L_0 + \alpha t + \beta t^2$ where α and β vary with concentration.[19] A similar law applies to the heat content of hydrogen bromide in sodium bromide solutions.[23] The integral heat of sodium bromide may be represented by the equation $\Delta H = -359m^{1/2}$.[21]

The heat of solution of one mole of the salt in 100 g. of water using an adiabatic calorimeter was found to be the same, 225 g.-cal.mol.$^{-1}$ ± 0·3%, whether the salt had been previously fused or purified by recrystallization although it had been stated that the value varied with the method of preparation of the salt.[24] Over the total range of solubility the integral heat of solution was found to be[25] 865 g.-cal.mol.$^{-1}$l.$^{-1}$ and could be expressed by the relation $L_S = -359m^{1/2}$.[21] The differential heat of solution was 620 g.-cal. mol.$^{-1}$, while the differential heat of dilution is 40·4 g.-cal.mol.$^{-1}$.[25] The heat of dilution extrapolated to infinite dilution is in water 0·01, in methanol 4·30, and in ethanol 2·65 kg.-cal.mol.$^{-1}$ These results were shown to be inconsistent with the Born–Bjerrum equation for the heat of solvation of the ions. The heats of transfer from one solvent to the other have also been calculated.[26] The heat of solution of $NaBr,2H_2O$ was found from e.m.f. measurements to be -2933 g.-cal.[27] The heat of solution in liquid ammonia at −33°C. varies linearly with concentration over the range 0·1–0·5M. owing to the considerable heat of dilution, which is 5600 g.-cal. for $C = 1$ and $C = 0$. The heat of solution extrapolated to infinite dilution[28] is 10,350 g.-cal.mol.^{1} though a value of 9500 g.-cal.mol.$^{-1}$ has also been reported.[29] The heat of the reaction $NH_4Br + NaNH_2 \rightarrow NaBr.am + 2NH_3(liq.)$ is −33 kg.-cal.mol.$^{-1}$.[29]

The integral heat of solution in formamide is given by the expression $\Delta H = -580 - 2100m$.[30]

The free energy of hydration of the ions has been calculated[31] as 163·2 and the heat of hydration as 170 kg.-cal.mol.$^{-1}$.[32]

The work of removing an anion or a cation from sodium bromide to infinity has been estimated as 4·81 and 4·36 ergs, respectively.[33]

The effect of concentration on the heat of transport of the ions has been determined; at 32°C. the value ranges from 415 to 940 g.-cal.mol.$^{-1}$ for M. and 4M. solutions respectively.[34]

The energetics of solid solutions of sodium chloride and bromide, including the heats of formation and evolution and the free energy, have been calculated on the basis of Wasastjerna's statistical theory over a range of temperatures and found to agree reasonably well with experimental values. The experimental heat of formation has a maximum value at 0·5 mole-fraction of 335 g.-cal.mol.$^{-1}$.[35-37] The heat of solution of the solid salt in liquid sodium calculated from the temperature coefficient of solubility is 24 ± 1 kg.-cal.mol.$^{-1}$.[7]

The free energy of solutions of sodium bromide in fused silver bromide was estimated from e.m.f. measurements between 450 and 620°C. as −17·48 kg.-cal.mol.$^{-1}$.[38] The heat of dilution, entropy and activity coefficients were also calculated and the results indicated a positive deviation from Raoult's law.

The specific heat of concentrated aqueous solutions of sodium bromide is found to obey the equations:-

$$\Phi C_p = -29{\cdot}715 + 20{\cdot}049m^{1/2} - 1{\cdot}625m \text{ at } 25^\circ\text{C.}$$
$$\text{and } \Phi C_p = -24{\cdot}467 + 16{\cdot}453m^{1/2} - 1{\cdot}034m \text{ at } 30^\circ\text{C.}$$

The deviation for 1M. solution was −0·08%.[39] The thermal conductivity of the crystalline salt was found to be 6×10^{-3} kg.-cal.cm.$^{-1}$°C.$^{-1}$sec.$^{-1}$ at 0°C.[40] The coefficient of linear thermal expansion of sodium bromide crystals is 46·5 $\times 10^{-6}$°C.$^{-1}$.[41] The cubic coefficient of expansion is $12{\cdot}4 \times 10^{-5}$ at 50°.[37]

The specific volume and coefficient of expansion of solutions in ethylene glycol have been determined for a range of concentrations. The apparent molal expansibility of the salt is negative, and increases with the concentration. Comparison with aqueous solutions indicates that structural changes in water largely determine the expansion in aqueous solution.[42]

The surface energy of the (001) face of sodium bromide crystals was determined as 118·7 ergs,[43] and that of molten sodium bromide measured by the maximum bubble pressure method was 108 ergs at 700° and 103 at 800°.[44] The surface tension of fused binary mixtures of sodium and potassium bromides was compared with values calculated from Guggenheim's equation for ideal binary mixtures and the small negative deviations from the calculated values were interpreted in terms of the differences in ionic radii.[44] The surface tension of saturated aqueous sodium bromide was determined[45] as 84 dynes cm.$^{-1}$ and over the concentration range 0·01–0·3M. values were found to agree with those calculated by a statistical thermodynamic method.[46]

For both aqueous and ethylene glycol solutions of propyl, butyl or *iso*amyl alcohol there is a definite buffer concentration of alcohol for which the surface tension is independent of the concentration of sodium bromide from 0·5–2·8M. A 4·0M. sodium bromide–0·011M. butyl alcohol solution has a constant surface tension of 68·5 dynes cm.$^{-1}$ from 0° to 80°C. while the equation $g = g_0 + \alpha\sqrt{C^3}$ for surface activity as a function of concentration holds for BuOH–NaBr–H_2O solutions at 0°, 20° and 40°C.[47] The buffer point of the system PrOH–NaBr–H_2O is at 0·004M. alcohol for 0–2·8M. NaBr.[48]

The dielectric constant of single crystals has been measured as 6·39,[49] and 6·1.[50] The dielectric strength is reported to be 1·0 mV./cm. but the precise significance of this is not explained.[51] The dielectric constant of solutions of sodium bromide plotted against molar concentration decreases to a minimum of 60·5 at a concentration of about 0·0035M., then increases and finally reaches a limiting value of 78·0.[52] This behaviour is attributed to binding of the solvent molecules by the ions and can be interpreted in terms of the basic Debye equations for a polar medium.[53]

From a study of the nuclear quadrupole couplings it is calculated that the sodium bromide binding has zero *s* character and is 99% ionic.[54]

The compressibility of crystalline sodium bromide measured by Bridgman's method using pressures up to 12,000 atm. was $5{\cdot}08 \times 10^{-12}$ at 30° extrapolating to $3{\cdot}9. \times 10^{-12}$ cm.^{2}dyne^{-1} at absolute zero. The change of compressibility with pressure independent of temperature was $25{\cdot}5 \times 10^{-12}$ and the average change of compressibility with temperature between 30° and 75° was $7{\cdot}5 \times 10^{-4}$°C.$^{-1}$.[55]

The average internal pressure of sodium bromide crystals was found[5] to be 85,000 kg.cm.$^{-2}$, from which were calculated values of the atomic diameters agreeing closely with those found by other methods.[56] Compressibilities calculated from crystal lattice constants agree well with these results[57] and a value of 5·914 abs.units was found for the specific inductive capacity.[58] The compressibilities of aqueous solutions have been measured at pressures up to 1000 bars. The apparent compression of the salt solution can be expressed by the equation:-

$$A = -\Delta p_w + \Delta p_v / x_1$$

where Δp_w and Δp_v are the partial compressions of water and salt respectively, x_1, x_2 are the weight fractions[59] and:-

$$A = 298{\cdot}9 \times 10^{-4}\,(x_2/x_1) + 190{\cdot}2 \times 10^{-4}\,(x_1/x_2)^{3/2}$$

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The apparent compressions of methanol solutions have been measured by the same method.[60]

The self diffusion coefficient D of sodium in sodium bromide crystals has been measured over a range of temperatures and the results compared with those calculated from the electrical conductivity and by means of the Einstein equation:-

$$\sigma/D = Ne^2/kT$$

where N is the number of ions of a given kind, e the electron charge, T the absolute temperature and k the **Boltzmann** constant. The Einstein relation is satisfied at temperatures above 400°C. but below this temperature the calculated results are too low.[61] The temperature dependence of diffusion may be explained by the Schottky-Wagner vacancy theory if the presence of impurities is taken into account, giving the relation:-

$$D = D_0 \exp \left(\frac{e + e'}{2}\right)/kT$$

where D_0 is 0·67 cm.^{2}sec.$^{-1}$ and $(e + e')/2$ is 1·53 for experimental data, the corresponding values for conductivity data being 5·98 and 1·68. In this equation e is the energy needed for a sodium ion to jump into a vacancy and e' is the work necessary to create a positive and a negative ion vacancy by moving ions to the surface. At low temperatures the equation becomes:-[62]

$$D = D_0' \exp(-e/kT)$$

where D_0' is 10×10^{-6}. The values of e calculated from this[62] and from other data[63] are 0·848 and 1·02 while e' is 1·68 and 1·66 eV., which are reasonable values. The coefficient of self-diffusion of a bromide ion in the crystal has been measured between 360° and 680° and above 450° the results can be expressed by:-

$$D_{\mathrm{Br}} = 50 \exp(-2{\cdot}02)/kT.$$

At low temperatures, in contrast to the results for diffusion of sodium ions, the measured values are 30–40 times smaller than those calculated from conductivity data. From this it is concluded that the existence of pairs of ions is unlikely.[64] The activation energy for migration of a sodium ion vacancy is 0·80 ± 0·03 eV. and that for bromide ion vacancy is 1·18 eV. The energy for formation of a separated pair of positive and negative ion vacancies is 1·68.[65] These figures agree closely with those calculated above from the diffusion of sodium ions. A calculation based on conductivity data gives support to the vacancy transport assumption for sodium bromide.[66]

The following values have been calculated for the Soret coefficient at 30, 40, 50 and 60°C. respectively:[34] 2·09, 2·26, 2·99 and $3{\cdot}42 \times 10^{-3}$. The value calculated[67] from e.m.f. measurements at 35°C. is 4×10^{-4}. The electro-osmotic effect has been studied over the concentration range 10^{-1} to 10^{-4}M. using a glass membrane. The results were interpreted in terms of a theory based on electrolysis and ion hydration.[68,69]

The decomposition potentials of fused sodium bromide were found to be 2·88V. at 765° and 2·85V.[70] or 2·83V.[71] at 800°. The potential for the liberation of sodium from sodium bromide in the system $AlBr_3$–NaBr–ethyl bromide is 3·5–3·8V. At low molecular ratios of sodium bromide to aluminium bromide only the decomposition potential of aluminium bromide was observed. At certain current densities and compositions a potential corresponding to decomposition of a complex ion was measured.[72,73] For sodium bromide dissolved in fused zinc bromide the potential is 1·18V.[74] The electrode potentials of many metals have been determined in fused salt mixtures such as NaBr–KBr, NaBr–$AlBr_3$, NaBr–AgBr.[75,76] The e.m.f. of cells of the Daniel type with electrolytes of fused $NaBr-AlBr_3$ have been measured with many metals as electrodes. The e.m.f. varies linearly with temperature.[77] A reversible glass–tin–sodium reference electrode has been described for potential measurements at high temperatures, and electrode potentials have been measured between silver metal and a sodium bromide–silver bromide mixture.[78] The contact potentials of a number of metals with aqueous solutions of sodium bromide have been measured.[79] Electrocapillary curves have been obtained for N. sodium bromide in methanol and the results indicate that the activity of the anion is the same as in water.[80]

Potential–time and polarization curves have been obtained with aluminium in sodium bromide solutions.[81]

The solubility of sodium bromide in water at 25°C. has been redetermined as[82] 48·22 as compared with an earlier value of 48·61.[83] The solubility at 39° is stated to be 53·6 ± 0·05.[84] The solubility of sodium bromide in water at various temperatures is given in Table II. The transition temperature is 50·2°C.[85]

TABLE II.- SOLUBILITY OF SODIUM BROMIDE IN WATER

Temperature °C.	Solubility g./100g.
0·00	44·47
35·00	50·48
45·21	52·66
50·21	53·80
60·17	54·10
75·44	54·42
91·95	54·83

Table III gives the solubility of sodium bromide in water in the presence of hydrogen bromide at 25°C.[82]

TABLE III.- SOLUBILITY OF SODIUM BROMIDE IN AQUEOUS HYDROGEN BROMIDE (g./100g. of solution)

HBr	NaBr	Total bromide
–	48·22	37·45
4·61	42·55	37·59
9·04	37·19	37·81
12·98	32·62	38·15
17·65	27·31	38·64

The solubility in liquid ammonia is quoted as 39·00 ± 0·01 at −0·1°C.,[86] 17·62 at −33·9°C.,[87] 11·24 **(g./100c.c. solution)** at −35°C. and 7·37 at −44·6°C.[88] The solubility increases from 11·76 at −44·5° to 137·0 at +25°C.[89]

The solubility in methanol[90] is given in Table IV: the salt is said to be non-alcoholated in this solvent.

The solubility has also been measured in methanol, ethanol and butanol at temperatures from 20–55°C.[91] The density and solubility at 25°C. are: in methanol 0·912 and 16·3; in acetonitrile 0·786 and 0·04; and in formic acid 1·375 and 19·3.[92]

The solubility in ethanol has been determined with the results given in Table V, the solid phase being NaBr throughout.[93]

The solubility of sodium bromide in acetone was found to be 1·190 × 10^{-3} moles per litre at 25°C.; lithium and calcium perchlorates increased this solubility much more than was indicated by the Debye–Hückel theory of

TABLE IV. - SOLUBILITY OF SODIUM BROMIDE IN METHANOL

Temperature °C.	Solubility (g./100g.)
0	17•3
10	17•0
15	16•9
20	16•8
30	16•5
40	16•1
50	15•8
60	15•3

TABLE V. - SOLUBILITY OF SODIUM BROMIDE IN ETHANOL

Temperature °C.	Solubility (g./100g.)
0	0•02445
10	0•02379
15	0•02343
20	0•02322
25	0•02314
30	0•02292
40	0•02276
50	0•02259
60	0•02312
70	0•02345

interionic attraction.[94] The solubility in acetone in the presence of sodium nitrate was found to be depressed by the common ion effect as occurs in water.[95]

The solubility in liquid sulphur dioxide is 0•0038 g./100g. of solution.[96] Sodium bromide is practically insoluble in mesityl oxide[97] and titanium tetrabromide.[98]

Relative rates of Soxhlet extraction of sodium bromide by various solvents have been measured;[99] 96% ethanol extracted 7g. and acetone 30mg. per hour. Acetic acid and ethyl ether did not dissolve sodium bromide.

The solubility of ethyl acetate in aqueous solutions of sodium bromide was determined by a turbidometric method over the temperature range 20°–40°; the results are given in Table VI.[100]

TABLE VI. - SOLUBILITY OF ETHYL ACETATE IN AQUEOUS SODIUM BROMIDE SOLUTIONS

NaBr molar concn.	Solubility of ethyl acetate g./100g. solution			
	20°	25°	30°	35°
0•1	8•12	7•79	7•45	7•12
0•2	7•94	7•59	7•24	6•89
0•3	7•73	7•57	7•01	6•65
0•4	7•56	7•18	6•81	6•43

The solubilities of benzene, naphthalene and biphenyl at 25°C. in 0•1M. aqueous sodium bromide are given by the relationship $\log S_0/S = KC_s$, where S_0 and S are the solubilities of the non-electrolyte in pure water and salt solution respectively and C_S is the concentration of salt. K has the values: for benzene 0•155, for naphthalene 0•169, and for biphenyl 0•209.[101]

The density of saturated aqueous solutions of sodium bromide is given in

Table VII.[85]

TABLE VII. - DENSITY OF SATURATED AQUEOUS SOLUTIONS OF SODIUM BROMIDE

Temperature °C.	Density
0·00	1·4957
35·00	1·5655
45·21	1·5950
50·21	1·6108
60·17	1·6073
75·44	1·5986
91·95	1·5915

The density of solutions of various concentrations at 25°C. is given in Table VIII.

TABLE VIII. - RELATION OF DENSITY AND CONCENTRATION FOR AQUEOUS SOLUTIONS OF SODIUM BROMIDE AT 25°C.

Normality	Density at 25°C.	
	Ref. 102	Ref. 103
0	0·99654	0·99707
0·99922	1·07195	-
1·1794	-	1·08330
2·01264	1·14289	-
2·9075	-	1·20339
3·00158	1·20790	-
3·99924	1·26947	-
4·1641	-	1·28124
4·99933	1·32775	-
5·1971	-	1·34108
6·02882	1·38241	-

The variation in density of sodium bromide solutions with temperature is given by the expression:-

$$d = 1{\cdot}7430\,(1 - 0{\cdot}00043291T),$$

where d is the density and T the absolute temperature: this is said to apply within ±0·04% between 18° and 40°C. Data are also given for the density of solutions in aqueous alcohol.[104]

The density of methanol solutions at 25°C. is given in Table IX.[105]

TABLE IX. - DENSITY OF SOLUTIONS OF SODIUM BROMIDE IN METHANOL

Concn. g.mol./1000g.	0·6142	0·3185	0·15895
d_4^{25}	0·83562	0·81169	0·80027

The density of a saturated solution in methanol is stated to be 0·912, in acetonitrile 0·786 and in formic acid 1·375.[92] The density of a 1·101M. solution in ethylenediamine is 0·984 at 15° and 0·974 at 25°.[106]

The fluidity of aqueous solutions of sodium bromide agreed with the following equations within 1% over the range 18°–40°C.:-[104]

$$\Phi_1 = -321{\cdot}224 + 1{\cdot}2204T$$
$$\Phi_2 = -2439{\cdot}676 + 3637{\cdot}1V,$$

where V, the specific volume, was $c - d \log (T_k - T)$. The viscosity increment in methanol solution,[105] K/c, where $K = (\eta_{sol.} - \eta_{alc.})/\eta_{alc}$, is given in Table X, V being the volume change in solution.

TABLE X. - VISCOSITY INCREMENT OF AQUEOUS SOLUTIONS OF SODIUM BROMIDE

Concentration (g.mol./1000g. of solution)	K	K/c	V
0·6142	0·367	0·598	26·1
0·3185	0·1936	0·607	26·8
0·15895	0·1028	0·646	42·8

The conductivities of single crystals and of compressed pellets of sodium bromide have been measured at temperatures from 440° to 740° with an error of ±8%. The values ranged from 0·66 and 0·85 × 10^{-6} for crystal and pellet respectively at 440° to 246 and 276 × 10^{-6} at 740°, the conductivity of the pellets being 15–20% higher than that of the crystal at the same temperature.[8]

A number of determinations have been made of the conductivities of sodium bromide in various solvents and the values of the limiting conductivities are given in Table XI. All values were obtained at 25°C. except where a different temperature is given in brackets.

TABLE XI. - CONDUCTIVITIES OF SODIUM BROMIDE IN VARIOUS SOLVENTS

Solvent	Λ_∞	Reference
Water	127·38	107
Water	125·85	108
Water	128·25	109
Methanol	106·7	110
Methanol	101·5	111
Methanol	104·8	113
Methanol	101·76	109
Methanol	101·5	112
Methanol	65·8 (32°C.)	114
Ethanol	46·3	110
Ethanol	44·9	113
Ethanol	44·85	115
Acetic acid	37·0 (30°C.)	116
Acetamide (fused)	40·3 (90°C.)	117
Dimethylformamide	83·4	118
N-Methylacetamide	21·0 (40°C.)	119
Hydrogen cyanide	343·8 (18°C.)	120

The equivalent conductivity in ethylenediamine is 10·8 at a concentration of 0·218M.[106]

The conductivity in mixtures of methanol and ethanol has also been measured.[121]

The change of conductivity with dilution has been expressed in some cases by empirical equations; in others the Kohlrausch or Debye-Hückel-Onsager equation has been found to apply.

In water $\Lambda = 128{\cdot}26 + 234C + 65C \log C$.

or $\Lambda = 128{\cdot}21 + 90C$.[109]

In methanol, $\Lambda = 101{\cdot}5\,(1 + 1{\cdot}70C)\exp(-2{\cdot}36C^{1/2} + 0{\cdot}12C)$ with 1·5% error for range 0–2N.[112]

In ethanol, $\Lambda = 44{\cdot}85 - 192C^{1/2}$ holds with accuracy over the range 0·6246 – 7·864

Use of the Debye–Hückel–Onsager equation to calculate the Kohlrausch parameter k gave rise to deviations from the observed value up to 33%.[115]
In hydrogen cyanide, $\Lambda = 343{\cdot}8 - 265{\cdot}5C^{1/2}$ with an error of 8–10%.[120]

An expression has been derived from fundamental principles for the equivalent conductivity in any solvent. Values calculated from this expression agree well with experimental values for sodium bromide in methanol.[114]

Kohlrausch's rule of the independent migration of ions has been confirmed for water,[109] methanol,[111] ethanol,[111] dimethylformamide[118] and *N*-methylacetamide.[119]

From conductivity data in acetic acid the ionic dissociation constant for sodium bromide was calculated to be $1{\cdot}3 \times 10^{-7}$.[116]

The effect of pressure on the conductivity of aqueous solutions has been measured over the range 1–10,000 kg.cm.$^{-2}$ A maximum was observed in the conductivity which cannot be caused by a change in the degree of dissociation. It was concluded that a large change in the diameter of the ions must occur at high pressures.[122]

The conductivity of silver bromide crystals has been measured over the temperature range 175–400° C. and the results used to calculate the concentration of vacancies in the lattice ('holes'),[123] the mobility ratio and the disorder association. Conductivities of sodium bromide in molten iodine bromide have been measured over a range of concentrations.[124]

When water or alcohol is added to a mixture of electrolyte and dioxan in a conductivity cell, at a certain actual concentration of polar liquid there occurs a sharp rise in current due to sudden dissociation of the electrolyte. For sodium bromide this critical concentration in mol.l.$^{-1}$ of dioxan is for water 2•69 and for alcohol 6•36.[125]

The electrolyte transport of water in 0•1N. NaBr was found to be 6•00 and the transport number of the cation was 0•486.[126] The ionic conductivities (relative mobilities) have been determined in a number of solvents and the results are given in Table XII.

TABLE XII. - IONIC CONDUCTIVITIES FOR SODIUM BROMIDE IN VARIOUS SOLVENTS

Solvent	Ionic conductivity		Temperature °C.	Ref.
	^{1}Na	^{1}Br		
Water	44•140	66•822	25	127
Water	43•0	67•0	18	120
Methanol	45•21	56•55	25	109
Methanol	49•4	57•3	25	110
Ethanol	21•8	24•6	25	110
Ethanol	24•0	21•0	25	128
Hydrogen cyanide	132•4	211•4	18	120

Ionic mobility has also been studied in ion exchangers using sodium bromide as the external electrolyte.[129]

From electrical conductivity data in homogeneous solid solutions of sodium bromide in silver bromide, the ionic radii have been calculated as Na 0•98A., Br 1•95A.[130] The radii calculated in the saturated solution, Na 1•21A., Br 2•20A., are larger than these but smaller than those found in dilute solution.[131] The effective radii of the hydration envelopes in dilute solution have been estimated as Na 1•57A., Br 2•05A.[132] The distance of closest approach of the ions has been calculated by a number of methods: from conductivity data 3•25A., from the osmotic coefficient 6•0A., from the ionic mobilities 3•00A. and from the atomic radii 2•90A.[133] The distance between the ions has also been calculated from the limit of full solvation.[134]

The hydration number has been estimated from vapour pressure data as 8 + 3 = 11 corresponding to 13·1 moles of water bound in a 9·90N. solution.[135] Cryoscopic determinations indicate that hydration corresponds to 12·9 molecules of water per ion pair in N. solution and to 15·3 molecules in 0·5M. solution.[136] Exact ebullioscopic data are consistent with the presence of $NaBr,9H_2O$ at the boiling point.[137] Co-ordination numbers of water molecules have also been evaluated from the ionic radii and the radius of the water molecules, the values being in very dilute solution Na 6, Br 8. This hydration envelope is believed to consist of liquid rather than 'frozen' water.[132] The volume of the water of hydration has been measured with an ultrasonic interferometer.[138] From dielectric constant measurements it is calculated that, under the experimental conditions, 162 moles of water are bound per mole of salt, this being equivalent to $8 \cdot 4 \times 10^3$ molecules per unit charge.[139]

Activity coefficients have been evaluated from both vapour pressure and e.m.f. measurements and the best values at 25°C. are given in Table XIII.

TABLE XIII. - ACTIVITY COEFFICIENT OF SODIUM BROMIDE IN AQUEOUS SOLUTION AT 25°C.

Molarity	Ref. 140	Ref. 141	Ref. 142	Ref. 143	Ref. 19
0·05	–	0·824	–	–	–
0·1	0·780	0·780	0·780	0·780	0·782
0·2	0·744	0·738	0·745	0·739	0·740
0·3	–	–	0·724	0·717	0·718
0·5	0·714	0·697	0·705	0·698	0·695
0·7	–	–	0·699	0·689	0·697
1·0	0·715	0·688	0·697	0·688	0·686
1·5	–	0·697	–	0·704	0·703
2·0	0·782	0·733	–	0·732	0·734
2·5	–	0·774	–	0·770	0·778
3·0	–	0·824	–	0·814	0·826
3·5	–	0·872	–	0·868	0·876
4·0	–	0·934	–	0·928	0·934

The coefficients of the Hückel equation were found to be[141] A 0·88, B 0·0383 and A 0·915, B 0·04.[144]

The activity coefficients found at various temperatures for a 2N. solution were[145] 25°C. 0·737; 35°C. 0·743; 45°C. 0·658; 50°C. 0·634. The chemical potentials have been calculated from vapour pressure data by three new methods.[146]

Other determinations of activity coefficients in moderately concentrated aqueous solution have been made.[147,148] The activity coefficient of sodium bromide in ethanol solution is given in Table XIV.[149,150]

The refractive index of the solid dihydrate is 1·5191 ± 0·0001, and that of the anhydrous salt 1·6439 ± 0·0001, the respective molecular refractions being given as 19·481 and 11·61,[5] and 17·64 and 11·10.[151] The refractive indices of prisms of the mixed salts sodium and potassium bromides have been measured at 66°C. in the ultra-violet and visible regions 2000–6000A.[152] The equivalent refraction in solution at infinite dilution has been determined by several investigators, the best value being 12·91.[102,103,153,154]

The increments of the refractive index per unit % increase in concentration have been determined and found to vary from 0·001410 at 4·97% to 0·001350 at 19·8%.[155]

The Faraday rotation of a single crystal of sodium bromide was measured

TABLE XIV. - ACTIVITY COEFFICIENT OF SODIUM BROMIDE IN ETHANOL SOLUTION

Molar concn.	Activity coefficient
0•0052	1•0
0•0104	0•94
0•03125	0•83
0•0625	0•76
0•125	0•678
0•25	0•597
0•5	0•50
1•0	0•41

in a magnetic field of 15,400 oersteds and the Verdet constant found to be 0•0621 and 0•123 min.cm.$^{-1}$oersted^{-1} at wave-lengths 5461 and 4358A. respectively. The corresponding magneto-optic anomalies were 0•86 and 0•88.[156] The magneto-optic rotation and optical dispersion have also been measured in solutions of various concentrations, the results being given in Table XV.[157,158]

TABLE XV. - MAGNETO-OPTIC ROTATION AND OPTICAL DISPERSION OF SODIUM BROMIDE IN SOLUTION

Molar concn.	Mol. mag. rotativity	Mol. dispersibility	Mol. refraction	Mag. opt. anomaly
1	45•5	43•60	13•29	0•95
3	43•5	41•60	13•13	0•93
4	42•0	41•05	13•06	0•92

The molecular light scattering by dilute solutions of sodium bromide has been investigated and the experimental Rayleigh constant 0•92 found to agree reasonably well with the theoretical value 1•00 calculated from Debye's equation.[159,160]

The photoelectric effect occurs between the wave-length limits 2210–2116A.[161,162] When crystals are prepared in the dark they are perfectly transparent to visible light, but after a slight exposure to ultra-violet light a narrow absorption band appears in the deep red.[163] *X*-Ray luminescence spectrograms have been recorded between the wave-lengths 2750–7000A.[164] Sodium bromide was found to be the only substance which emitted *X*-ray fluorescence with bactericidal properties.[165] In common with other sodium halides it is able to change the yellow-green phosphorescence of zinc sulphide to blue;[166] the line 6495A. is weakened and a new line appears at 6545A.[167] The effect of nitrite ions on the absorption spectrum of sodium bromide has been studied.[168]

The magnetic susceptibility of solid sodium bromide has been measured as 4•04 x 10^{-7},[169] and 3•3 x 10^{-7},[170] Another investigator using different methods[171] found values of 3•568 and 3•706 x 10^{-7}.

A number of investigations have been made of binary and ternary systems containing sodium bromide. Systems containing water may first be considered. The vapour pressure curves of the systems $NaBr,2H_2O$–NaBr–vapour and NaBr–solution–vapour have been determined from 10° to 50•6° C., the vapour pressure of the system $NaBr,2H_2O$–solution–vapour from 50•6° to 100°C.[172] A number of singular folds have been observed in the systems Na_2O–HBr–H_2O and NaBr–NaOH–H_2O. In neutral solution the transition $NaBr,2H_2O \rightarrow NaBr$ takes place at 50•7°C. but dehydration occurs at lower temperatures in the presence of base or acid. Thus dehydration occurs at 44•5°C. with 5•13% NaOH or 11•49% HBr, and at 25°C. with 15•91% NaOH or 41•38% HBr.

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Similarly the transition point for $NaBr,2H_2O \rightarrow NaBr,5H_2O$ is −22•0°C. in neutral solution, −28•7°C. with 5•52% NaOH and −27•0°C. with 9•12% HBr.[173] The system $NaCl-NaBr-H_2O$ has two fields of solid solutions $Na(Cl,Br)2H_2O$ and Na(Cl,Br), a field of ice and one of $NaBr,5H_2O$. There is a eutectic at −29•2°C. of composition NaBr 74•95, NaCl 25•05 and H_2O 84•5 moles.[174,175] Salt temperatures, *i.e.* temperatures at which solid just begins to crystallize, have been plotted for this system.[176] The method of spiral co-ordinates has been applied to it with success.[177] The salts NaBr–NaCl in the presence of 6•61M. aqueous NaOH at 35°C. form a continuous series of solid solutions with no miscibility gap.[178] In the system $NaBr-KBr-H_2O$ there are six fields of crystallization meeting in a ternary point at −32•0°C. of composition NaBr 91•34, KBr 8•66, H_2O 850 moles.[174] Solubility, viscosity and specific gravity isotherms of this system consist of two branches which meet at a point of composition, in weights % for KBr and NaBr, of 4•86 and 41•05 at 0°C. and of 7•07 and 44•30 at 25°C. respectively. The only solid phases indicated are KBr and $NaBr,2H_2O$. The specific gravity and viscosity form sharp maxima at this point at 1•5669 and 4•6423 at 0°C. and at 1•5778 and 2•6234 at 25°C. respectively.[179] Neither compounds nor solid solutions are formed by the system $NaBr-NaNO_3-H_2O$.[180] In the system $NaIO_3-NaBr-H_2O$ two double salts were formed, $2NaIO_3,3NaBr,15H_2O$ existing up to about 40°C. and $2NaIO_3,3NaBr,10H_2O$ at higher temperatures.[181] The system $NaBr-NaCl-NH_3$ has a eutectic at 0°C. of composition 4•25% NaCl, 35•42% NaBr and 60•44% NH_3.[182] The system $NaBr-H_2O$–*iso*propanol has also been studied.[183] The system $NaIO_3-NaBr-H_2O$ showed the presence of two double salts $2NaIO_3,3NaBr,15H_2O$ existing up to 40°C. and $2NaIO_3,3NaBr,10H_2O$ at higher temperatures.[184]

The melting point curve of the binary system NaBr-KBr has been determined in a study of the correlation of the lowering of the melting point with crystal parameters.[185]

The binary system Na-NaBr has a monotectic a few degrees below the melting point of the pure salt and a consolute temperature of 1090°C. The mutual solubility of the salt and of sodium in the liquid phase was measured up to about 25 mole %.[186] The details of the crystallization surfaces of the systems (Na,K)(Br,I), (Ag,Na)(Br,Cl), have been determined. The latter system has a single crystalline surface and four binary salts form a continuous solid solution. The thermal value is 5•1 kg.-cal. and indicates that the stable pair is AgBr and NaCl. The ternary system NaCl–NaBr–NaI has also been studied.[187]

In the absence of solvents the reciprocal system $KF + NaBr \rightleftharpoons NaF + KBr$ could be divided into two independent ternary systems: (1) NaF + KBr + KF with a ternary eutectic point at 570°C., and (2) NaF + KBr + NaBr with fields NaF and solid solutions of bromides. There were three fields of crystallization, one field of continuous solid solutions and two fields of the components NaF + KF.[188] The system $NaBr + Na_2CO_3$ is a simple eutectic system but the reciprocal system $(Na,K)(Br,CO_3)$ is divided into two fields of solid solutions of carbonates and bromides, the latter showing a ternary eutectic at 575°C.[189] The reversible reciprocal system $(Na,K)(Br,NO_3)$ shows three fields of crystallization, continuous solid solutions of NaBr-KBr occupying 91% of the total area, continuous solid solutions of $NaNO_3-KNO_3$ and a field of KNO_3-NaBr occupying 1% of the area.[190] The reciprocal system (Na,K)(Br,OH) has six crystallization fields, four of the components and two of the compounds KOH, KBr and NaOH,NaBr. Two of the five triple points are eutectic, at 170° and 250°C.[191]

The system $HgBr_2-NaBr$ has a eutectic at 232°C., 8•5 mol. % NaBr and transition points at 243° and 288°C. corresponding to the compounds $HgBr_2$, NaBr and $HgBr_2,2NaBr$.[192]

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Studies have also been made of the melting point diagrams of the systems, Na_2SO_4-NaBr,[193] AgBr-NaBr,[194] $AlBr_3$-NaBr[195] and RbBr-NaBr,[196] NaBr-Na_2CO_3.[197]

Single crystals of NaBr-$2H_2O$ melted inhomogeneously at the transition point 50·6°C. with formation of cubic crystals of the anhydrous salt, but when immersed in liquid paraffin homogeneous melting occurred at 80°C.[198]

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Chemical Reactions

From kinetic studies the absorption of gaseous chlorine by aqueous solutions of sodium bromide is found to occur in two stages, one a chemical displacement reaction, the other a simple absorption of chlorine. At low bromide concentrations the chemical reaction is insignificant.[1]

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Microwave radiation absorption has been used to show that water of crystallization in $NaBr,2H_2O$ is not in the liquid state.[2]

Much attention has been devoted to reactions and equilibria in anhydrous salts at high temperatures. The following is a typical reaction occurring when mixtures of sodium and potassium halides are fused:-[3]

$$30KCl + 20NaBr + 20KBr + 30NaCl \rightarrow 40KBr + 10KCl + 50NaCl$$

The system $KF + NaBr \rightleftharpoons NaF + KBr$ was found to be very complex; the heat of reaction is 11·6 kg.-cal., indicating that equilibrium is shifted towards the right, and the system could be divided into two independent ternary systems with a ternary eutectic at 570° C.[4] The thermal effect of the exchange reaction, $2NaBr + K_2CO_3 \rightleftharpoons Na_2CO_3 + 2KBr$, is 1·8 kg.-cal.equiv.$^{-1}$, and equilibrium is shifted to the right.[5] The reaction, $Na + KBr \rightleftharpoons NaBr + K$, has an equilibrium constant 28·8 at 800° C.[6]

The exchange reaction between propyl bromide and sodium bromide containing isotopically labelled bromine has been shown to follow a simple second order law, with $k \times 10^4$(0·1M. solution) 0·213, 2·13, 8·4 and 36 l.mol.$^{-1}$ sec.$^{-1}$, at 35, 61, 79 and 100° C. respectively. The activation energy is 18·0 kg.-cal.mol.$^{-1}$ which is in agreement with the activated complex theory.[7] The exchange reaction between allyl bromide and labelled sodium bromide takes place 25–30 times faster, $k \times 10^4$ being 0·6, 2·6, 12·5 and 46 at 10, 20, 40 and 61° C. The increased rate is also shown[8] by the lower value of the activation energy, 15·5 kg.-cal.mol.$^{-1}$ More thorough kinetic studies with ethyl bromide proved definitely that the reaction proceeded *via* the intermediate complex Br^X – EtBr.[9] The reaction constants for methyl and ethyl bromides at 50° C. are $k \times 10^4$, methyl 19·9, ethyl 1·7, the respective activation energies being 17·5 and 18·0 kg.-cal.mol.$^{-1}$.[10]

Sodium bromide forms stable addition compounds with betaine,[11] with dimethyloctylbetaine[12] and with sodium allyl sulphonate.[13]

The following equilibrium constants were found for the several salt pairs: NaCl–KBr 1·75 at 769°, NaBr–KI 10·02 at 777°, AgI–NaBr 4·12 at 705° and 2·89 at 754° C.[14] The distribution of sodium between molten sodium bromide and molten cadmium indicated that sodium dissolved in the salt was atomic.[15] The distribution of sodium between amalgam and solutions of KBr–NaBr suggested that the two salts were not equally dissociated at equivalent concentrations.[16] The systems NaOH–NaBr, NaOH–NaBr–NaI have also been studied.[17] When an equimolecular mixture of sodium metaphosphate and sodium bromide is heated to 650°–750° C. in the presence of air, bromine is liberated:-

$$2NaBr + Na_2P_2O_6 + \tfrac{1}{2}O_2 \rightarrow Na_4P_2O_7 + Br_2.$$

When heated below 400° C. the bromide acts merely as a catalyst in the polymerization of the metaphosphate.[18]

The equilibrium constant, $K = (N_{HBr} - P_{HCl})/(N_{HCl} \quad P_{HCl})$, of the heterogeneous gas reaction $NaCl + HBr \rightleftharpoons NaBr + HCl$ is 4·69 at 850° C. and 4·14 at 950° C. The solid phase is an ideal solution of the two salts. The heat of reaction is –3400 g.-cal.[19]

The equilibrium constant for the reaction:-

$$(Na,K)Cl + \tfrac{1}{2}Br_2 \rightleftharpoons (Na,K)Br + \tfrac{1}{2}Cl_2$$

has been derived theoretically as:-

$$\ln K_{K,Na} = N_{Na} \cdot \ln K_{Na} + N_K \ln K_K$$

where K_K and K_{Na} are the constants for the reaction with only one cation present.[20]

Metallic sodium may be obtained by electrolysis of sodium bromide in ethylenediamine.[21]

A number of association compounds are formed by sodium bromide and other metallic salts. Thus polarography of fused mixtures of zinc sulphate and sodium bromide indicates the existence of $ZnSO_4,2NaBr$.[22] An association complex appears to be formed with molten mercuric bromide[23] while complexes of the type $(AlBr_3)_m\ (NaBr)_n$, $(n>m)$ are deduced from ebullioscopic determinations in ethyl bromide solution.[24,25] Ion pairs are formed with cerous ion Ce^{3+}, K being 1·19 at 0·9M. NaBr.[26] The complex $HgCl_2,NaBr$ is stated to be stable in 0·005M. aqueous solution.[27,28] Periodicity in the interfacial tensions of a series of solutions of mercuric bromide and sodium bromide in butyl acetate is interpreted as proving the existence of many complexes (up to seven) of the type $n\ NaBr,HgBr_2$.[29]

Freezing point determinations have confirmed the formation of $NaBr_3$, the dissociation constant being 0·0441 at -0·65°C. and the calculated heat of formation 1976 g.-cal.[30] The solubility of iodine in solutions of sodium bromide suggests that $NaBrI_2$ is formed.[31]

Although sodium bromide usually crystallizes in the cubic system, dendritic crystallization may occur on slow evaporation of an aqueous solution particularly if gelatin or agar has been added. Formation of dendrites is, however, suppressed by the addition of ferric, cobalt or nickel chlorides to the solution.[32]

From aqueous solutions of sodium bromide and sodium chloride containing less than 88% of bromide, cubic mixed crystals are obtained at 6–8°C. containing less than 22% of sodium bromide and no water. If, however, the original solution contains more than 88% of bromide, the crystals are monoclinic and have the composition $Na(Cl,Br),2H_2O$.[33] The heat of formation of mixed crystals of sodium and potassium bromides is −0·713 kg.-cal. and this may explain their decomposition with decreasing temperature.[34] Certain mixed crystals show a turbidity on cooling and heating to definite temperatures but the system lithium bromide and sodium bromide exhibits turbidity over a very short range of composition.[35] Mixed crystals of sodium bromide and sodium chloride containing 10–12% of potassium hydroxide have been prepared.[36]

Oriented overgrowths are obtained by evaporating solutions of sodium bromide on freshly cleaned surfaces of galena. This oriented crystallization takes place at different temperatures for different varieties of galena[37] and depends on the degree of supersaturation of the bromide solution. The necessary supersaturation calculated from the work of separation of ions from the crystal agrees well with experimental values.[38] At temperatures above 50·7°C. the supersaturation is too small for sodium bromide to crystallize on to galena.[39] Such overgrowths can be observed microscopically by placing a drop of salt solution on the substrate.[40] Similar oriented overgrowths have been observed on sphalerite, rutile, magnetite[41] and felspar,[42] and by sublimation in high vacuum at high temperatures on to orthoclase,[43] mica,[44] silver[45] and alkali halides.[46] Electron diffraction studies in the last three cases have thrown some light on the mechanism of crystallization. This phenomenon may also be operative in the sorption of sodium bromide by crystalline precipitates such as silver bromide,[47] barium sulphate[48] and lead sulphide.[49]

Lead sulphide precipitated from solutions containing sodium bromide contained 9·6% of bromine but only a trace of sodium, indicating that the precipitate contained $PbS,PbBr_2$ rather than a solid solution of NaBr in PbS. Solid solutions may be formed, however, if the precipitate is allowed to stand in contact with the mother liquor.[50]

Sodium bromide in common with other alkali halides was found to retard the precipitation of calcium tartrate when the concentration of the salt was greater than that of the tartrate.[51]

Sodium bromide catalyzes the oxidation of carbon monoxide by nitrous oxide at 550–600°C. with simultaneous emission of the sodium resonance line.[52]

The distribution of thallium has been determined in sodium bromide crystals slowly precipitated from their saturated solutions at 95°C.[53]

Several studies of the neutral salt effect have included sodium bromide. The concentration of hydrogen ions in solutions 0·1N. in HCl and 0, 1, 2, 3 and 4N. in sodium bromide was 0·096, 0·140, 0·222, 0·438 and 0·800 respectively: the measurements were made by means of a hydrogen electrode against a calomel electrode.[54]

The effect of concentration of the salt on the rate of inversion of sucrose[54] and the rate of hydrolysis of ethyl acetate[55] has also been measured. The reaction constant increases with increasing concentration of sodium bromide and also as the reaction progresses, indicating some inhibition. Sodium bromide has also been included in series of salts in investigations of the salt effect on the hydrolysis of methylal and the activity coefficient of *p*-nitraniline,[56] the lowering of surface tension by anionic and cationic detergents[57] the carbonate–bicarbonate and phosphate equilibria,[58] the ionization constant of acetic acid,[59,60] the viscosity of sucrose solutions,[61] the activity coefficient of pyridine,[62] micelle formation in colloidal electrolyte solutions[63] and on the catalytic decomposition of hydrogen peroxide.[64]

Sodium bromide has been shown to catalyze the autoxidation of thiosulphate.[65]

Keratin absorbs appreciable amounts of sodium bromide[66] from solution, the bromide ion being mainly adsorbed from dilute solutions.[67] Addition compounds with amylose have been prepared by ion exchange.[68]

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Applications

Sodium bromide crystals containing silver or thallium have been used for scintillation counting of α and β particles.[1] The salt may also be used as an

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electrolyte in a primary cell suitable for delivering small currents.[2] The high density of sodium bromide solutions has been utilized in preparing a manometer fluid[3] and in increasing the rate of oil production from oil wells.[4] Sodium bromide added to a tanning bath was found to increase the firmness and hardness of leather and to raise the shrink temperature.[5] Sodium bromide was efficient in raising the yield of ethylene oxide by preventing the formation of hot spots in a catalyst.[6] Solutions of the salt have been found to enhance the rate of growth of quartz crystals.[7]

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SECTION XXVIII

SODIUM IODIDE

By F. CALL

Production and Preparation

Sodium iodide is prepared commercially by the interaction of ferrosoferric iodide, Fe_3I_8, produced by the action of iodine on moist iron, with sodium carbonate solution. After filtering off the carbonates of metals and precipitating sulphate by barium hydroxide, the solution is concentrated and allowed to crystallize.[1,2]

The high cost of iodine has stimulated interest in recovery processes. Thus iodine can be recovered from adsorptive carbon by boiling with sodium carbonate and subsequently reducing any iodate by sodium sulphite and bisulphite,[3] zinc powder[4] or carbon at an elevated temperature.[5] Iodine can be recovered from waste iodide solutions by precipitating with chlorine, suspending the iodine in water and treating with sulphur dioxide until the solution is colourless, this process being repeated several times if required. The solution is neutralized with lime, acidified and treated with barium iodide to precipitate sulphate. After adding the calculated quantity of sodium carbonate and filtering, crystallization of the solution yields sodium iodide of commercial purity.[6]

Sodium iodide can be purified by precipitating sulphate with barium iodide, adding hydrogen peroxide to oxidize ferrous iron and precipitating alkaline earths as carbonates by adding sodium carbonate. The filtrate is acidified to pH 6·5 by means of hydriodic acid, filtered to remove aluminium, magnesium and silicon, brought to pH 1·0 and finally concentrated and crystallized.[7] Purification for pharmaceutical purposes is similarly effected.[8] Apparatus has been described for the preparation of sodium iodide by the electrolysis of sodium iodate.[9]

The hot springs at Mondorf-Etat, Luxemburg, have been found to contain 0·00069 g. per l. of sodium iodide.[10]

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Physical Properties

Sodium iodide crystallizes in the cubic system, the unit-cell dimension (*a*) being 6·47 ± 0·01A.[1] No transition from a face-centred to a body-centred lattice occurs under hydrostatic pressures up to 50,000 atm., in agreement with prediction from the lattice constants.[2] Standard *X*-ray diffraction powder patterns have been prepared.[3] Photographs of the dehydration figures of dehydrated crystals have been published, but their interpretation is not clear.[4]

The density[1] of the crystal is 3·62, the Brinell hardness 8·4 and the plasticity coefficient[5] 0·0086. The surface energy of the (001) face has been calculated to be 118·7 ergs per sq. cm.[6] The melting point has been given as 660°C.[7] and 661°C.,[8,9] and the boiling point as 1300°C.[7,8] Vapour pressures at temperatures within 300°C. of the boiling point can be calculated from the equation:-[5]

$$\log P_{\text{atm.}} = -(39{,}400/4{\cdot}57T) + 5{\cdot}490.$$

The salt is stated to be practically completely dissociated at the boiling point, in accordance with the equation:-[8]

$$\log P_{\text{Na}}.P_{\text{I}} - \log P_{\text{NaI}} = -(16{,}800/T) + 1{\cdot}75T + 3$$

The lattice energy has been calculated as[10] 166·4 and 163·9 kg.-cal.mol.$^{-1}$ and from the latter value the entropy of the crystal is 36·3 and of the vapour 67·6 g.-cal.°C.$^{-1}$.[11] The heat of sublimation, calculated from the lattice energy and the heat of formation, is 51 kg.-cal.mol.$^{-1}$.[12] From the vapour pressure the heat of sublimation is calculated as 39, of fusion as 5, and of formation of the solid as 77 kg.-cal.mol.$^{-1}$.[7]

The free energy of formation, calculated from e.m.f. data for the reaction:-

$$\text{Na} + \tfrac{1}{2}\text{I}_2(\text{s}) = \text{NaI}(\text{s})$$

was $\Delta F^\circ_{298} - 68{,}465$ g.-cal. and the heat of formation, is $\Delta H^\circ_{298} - 69{,}700$ g.-cal.[13]

The apparent molal heat capacity in aqueous solution at any molal concentration *m* of salt at 25°C. up to 2·5 molal, can be calculated by means of the equation:-

$$\phi_c = -25{\cdot}0 + 16{\cdot}6m^{1/2}$$

The partial molal heat capacity is given by:-

$$C_p = -25{\cdot}0 + 24{\cdot}9m^{1/2}$$

and the heat capacity of a given solution in g.-cal. per g. of solution by:-

$$c_p = (1000 + m\phi_c)/(1000 + 149{\cdot}9m),$$

all values being g.-cal.mol.$^{-1}$ For the temperature range 18–25°C. $d\phi_c/dT = 0{\cdot}2857$.[14] The integral heat of solution has been measured as 2595 g.-cal. mol.$^{-1}$ and the differential heat of solution as 1610 g.-cal.mol.$^{-1}$.[15,16]

The heat of solution in water is given as 1·61, in methanol 7·52 and in ethanol 5·80 kg.-cal.mol.$^{-1}$.[17] The heat of solution in liquid ammonia at -33·4°C. is 17·5 kg.-cal.mol.$^{-1}$.[18] The integral heats of solution in various organic solvents have been measured at 0·04 molar concentration, the values being acetone (0·027M.) 9·56, methyl ethyl ketone 8·66, acetonitrile 6·74, allyl alcohol 8·15, pyridine 12·2, piperidine 10·15. In formamide the equation $L_s = -7600 - 2500m$ is found to hold.[19]

The free energy of hydration of the ions is 156·3 kg.-cal.mol.$^{-1}$,[20] the heat of hydration being[21] 161 or 159·8 kg.-cal.mol.$^{-1}$.[16] The heat of interaction between the ions and 1 mol. of water[21] is Na, 16·3 and I, 7·9 kg.-cal.g.ion^{-1}. The heat of dissociation in benzonitrile has been calculated from the dielectric constant of the solvent and conductivity data at 0, 25, 50 and 70°C., the values being 10, 14, 11 and 10 kg.-cal.mol.$^{-1}$ respectively.[22] The following heats were also calculated for this solvent: heat of removing from benzonitrile to vacuo 114; heat of dissociation in vacuo 126; heat of solvation 239; heat of solvation per anion 72; per cation 167; all in kg.-cal.mol.$^{-1}$.[22]

The coefficient of thermal expansion of crystals has been calculated from the crystal properties[23] as $45{\cdot}5 \times 10^{-6}$°C.$^{-1}$, agreeing well with the experimental value of $48{\cdot}8 \times 10^{-6}$°C.$^{-1}$

The specific volume of sodium iodide in aqueous solutions between 20° and 40°C. has been determined and found to fit the equation:-

$$\phi_2 = 0{\cdot}23407 + 0{\cdot}02479 x_2^{1/2}/x_1^{1/4}$$

where x_2 and x_1 are the weight fractions of salt and solvent respectively. The apparent thermal expansion can be calculated from:-

$$\Delta T_{\phi_2} = A + B(t - 30) + C(t - 30)^2$$

where the coefficients A, B and C vary with the concentration.[24] Comparison of results in methanol and glycol with those in water indicate that the expansion in aqueous solution is largely determined by structural changes in the water.[25]

The surface tension of solutions of sodium iodide has been studied by a loop method over the concentration range 0·01 to 0·3N. with a precision of 0·001%. The surface tension increased steadily with concentration.[26] Difficulties were encountered in determining the surface tension of solutions by a disc technique owing to the catalytic effect of the copper disc in liberating hydrogen iodide.[27]

The dipole moment calculated from conductivity data in benzonitrile is $1{\cdot}24 \times 10^{-17}$ e.s.u.[22] while the value measured by the molecular ray method at 975°C. is $4{\cdot}9 \times 10^{-18}$ e.s.u.[28]

The dielectric constant of the crystal is 6·15.[29] The dielectric constant of aqueous solutions has been measured by the ellipsoidal method at low frequencies at various concentrations. The curve showed two sharp minima at concentrations of 0·001 and 0·003%.[30] The minima shifted towards higher concentrations with increasing frequency. It is suggested that at the minima all the water molecules are bound by the ions as an ion-sheath of oriented water dipoles. At higher frequencies, the time required for the formation of such oriented dipoles would be too long and no minimum should occur.[31] The dielectric constant measured at frequencies of $2{\cdot}5 \times 10^5$ c/s. was in fact constant and independent of the concentration between 0 and 0·025N.[32] Using a ballistic method of measurement, the change of dielectric constant at high frequencies at concentrations below 0·01N. was found to obey the equation:-

$$D = D_0(1 + 0{\cdot}047C^{1/2} - C),$$

in accordance with the Debye–Falkenhagen theory, while at higher concentrations the equation:-

$$D = D_0(1 + 0{\cdot}095C^{1/2} - 1{\cdot}45C)$$

applied.[33] Curves showing the variation of dielectric constant with concentration have also been obtained by a decrement method.[34] The dielectric strength is reported as 0·7 mV.cm.$^{-1}$ but the significance of this is not explained.[35,36]

The specific inductive capacity of the molecule has been calculated as 6·031 abs.units.[37]

The compressibility of the solid[37-39] has been calculated as 6·9, 6·936, $6{\cdot}94 \times 10^{-6}$. Formulae have been derived for the variation of compressibility of aqueous solutions with concentration. The results agree closely with experimental values. Under 1 atm. pressure at 18°C. the compressibility is $42{\cdot}7 \times 10^6$ for 9·51% solution and $39{\cdot}7 \times 10^6$ for 18·75%.[40] The compressibilities in methanol and glycol have also been measured[41] and equations are given for water in addition to the two organic solvents.

A number of measurements have been made of the diffusion coefficients of the ions in aqueous solution at 25°C. and the results are given in Table I.

TABLE I. - DIFFUSION COEFFICIENTS OF THE IONS OF SODIUM IODIDE

Molar concn.	$D_{Na} \times 10^5$ cm.^{2}sec.$^{-1}$	$D_I \times 10^5$ cm.^{2}sec.$^{-1}$	Ref.
10^{-4}	1·435	-	42
0·1	1·274 ± 0·015	1·87 ± 0·03	43
1·0	1·264 ± 0·015	1·735	43
10^{-4}	1·445	-	43
5×10^{-4}	-	2·035	43
$\rightarrow 0$	-	1·73 ± 0·025	44

The values calculated from the Nernst equation at 10^{-4}M. were D_{Na} $1{\cdot}34 \times 10^{-5}$, D_I $2{\cdot}04 \times 10^{-5}$ cm.^{2}sec.$^{-1}$.[43] The integral diffusion coefficient at 25°C. was found to vary from $1{\cdot}554 \times 10^{-5}$ cm.sec.$^{-1}$ at 0·0419M. to $1{\cdot}785 \times 10^{-5}$ at 3·439M. The differential coefficient also varied from $1{\cdot}616 \times 10^{-5}$ at infinite dilution to $1{\cdot}992 \times 10^{-5}$ at 3·5M.[45]

The Soret coefficient of thermal diffusion was measured in 0·05M. solution at average temperatures of 30, 40, 50 and 60°C. with a temperature difference of 17°C., the values being $D^1/D \times 10^3$ 0·43, 1·14, 1·26 and 2·46 respectively.[46] The heat of transport at 1, 2, 3 and 4M. at 34°C. was 17·4, 34·6, 56·8 and 82·2 g.-cal.mol.$^{-1}$:[46] with 0·001N. solutions the Soret coefficient and heat of transport have been determined as $-0{\cdot}8 \pm 0{\cdot}1 \times 10^{-3}$°C.$^{-1}$ and -0·7 kg.-cal.mol.$^{-1}$ for iodide ion and 0·4 kg.-cal.mol.$^{-1}$ for sodium ion.[47]

The decomposition potential of the fused salt was found to be 2·30V.[48] Electrode potentials have been measured between a number of metals and fused sodium iodide and NaI-AlI$_3$ and decomposition potentials computed.[49] A reversible glass-tin-sodium reference electrode has been described for potential measurements at high temperatures, and electrode potentials have been measured between silver and sodium iodide-silver iodide mixtures.[50] Determinations have been made of the contact potentials between various metals and aqueous solutions of sodium iodide[51] and also of the interfacial distribution potential between immiscible liquids containing the dissolved salt.[52] Electrocapillary curves have been obtained for solutions in water, methanol and ethanol. The curves indicate that activities are similar in all solvents studied.[53] Polarographic studies have been carried out in anhydrous acetonitrile with a supporting electrolyte of 0·1M. tetrabutylammonium iodide. The diffusion current at a concentration of 10^{-3} molar was 3·18 microamp. the half-wave potential -1·25V. and the reduction potential -2·259V.[54] The adsorption of sodium bromide from aqueous and acetone solution on to silver iodide has been measured electrometrically and the electrical capacity of the molecular layer on the silver iodide calculated.[55] Potential-time and polarization curves have been obtained with aluminium in sodium iodide solution. The potentials become more positive with time.[56] Measurements of the electro-osmotic effect have been made at various concentrations using a porous glass membrane and the effect is explained in terms of electrolysis and ion hydration.[57]

The solubility of sodium iodide in water at different temperatures[58] is given in the following Table.

Refs. p. 969

TABLE II. - SOLUBILITY OF SODIUM IODIDE IN WATER

Temp. °C.	Solubility g./100g.
0·00	61·54
35·0	66·35
50·02	69·42
63·12	72·95
67·93	74·76
70·87	75·02
75·40	74·82
92·23	75·05

The transition point of the dihydrate is 68·1°C.[58]

The solubility at 20°C. in solutions 0 to 15·21N. in caustic soda has also been determined. The curves show a discontinuity at 8·20N. NaOH, and 6·92N. NaI, which marks the transition from dihydrate to anhydrous salt.[59]

The solubilities at different temperatures in methanol,[60] acetone[61] and methyl ethyl ketone[61] are given in Table III.

TABLE III. - SOLUBILITY OF SODIUM IODIDE IN CERTAIN ORGANIC SOLVENTS

Temp. °C.	Methanol	Acetone	Me Et Ketone
-70	-	-	7·3
-60	-	-	10·0
-50	-	-	14·0
-20	-	5·5	-
-10	-	7·8	22·8
0	-	11·8	20·1
10	0·650	18·2	17·4
20	0·729	30·0	15·0
25·7	-	40·7	-
30	0·814	39·2	12·7
40	0·807	35·6	10·7
50	0·801	32·0	8·9
60	0·794	28·6	7·4
70	-	25·1	6·2
80	-	21·8	-

The following figures for solubility (g./100g. solution) in acetone have been recorded[62] but these differ markedly from the values already quoted[61] which are themselves consistent with earlier values: 9·9° 15·4, 16·7° 20·1, 20·0° 23·0, 23·0° 25·5, 25·0° 27·3, 26·0° 28·2, 29·0° 27·6, 32·0° 26·9, 35·90° 26·2, 39·9° 25·1, 50·0° 23·1.

The following salt solvates are formed with the transition points stated: NaI,3MeOH, 27·4°C.,[60] $NaI,3Me_2CO$, 25·7°C. and NaI,3MeEtCO, -30°C.[61]

The solubilities in various non-aqueous solvents are given in Table IV.

Under the conditions of Soxhlet extraction, sodium iodide is not dissolved by ethyl ether but is readily soluble in methyl alcohol, ethyl alcohol and acetone. With ethyl acetate, in which the salt is more soluble at low than at high temperatures, 2·3 g. was extracted in 1 hr.[68]

The solubility has also been determined at 200°C. in aluminium iodide.[69]

The effects of dissolved lithium perchlorate,[70] lithium chloride[71] and sodium thiocyanate[71] on the solubility of sodium iodide have been studied. Two effects are distinguished, one due to interionic attraction, the other to a

TABLE IV. - SOLUBILITY OF SODIUM IODIDE IN VARIOUS NON-AQUEOUS SOLVENTS

Solvent	Solubility	Temp. °C.	Ref.
Methanol	72·0	25	63
Ethanol	42·57	25	64
*iso*Amyl alcohol	16·32	25	13
Acetonitrile	26·5	25	63
Formic acid	62·7	25	63
Ammonia	56·88	0	65
Ammonia	51·3	-35	66
Ammonia	44·8	-42·2	66
Sulphur dioxide (liquid)	1·59	25	67

salting out action, and the results agree satisfactorily with an equation derived by Brønsted.

The solubility of ethyl acetate in aqueous solutions of sodium iodide was determined by a turbidometric method over the temperature range 20°–40°C. and the iodide concentration 0·1–0·4 molar.[72] The distribution ratio of sodium iodide between ethylene glycol and ethyl acetate has been measured at 30°C.[73]

The densities, and the apparent and partial molal volumes of solutions at 25°C., have been determined by a magnetic float method at different concentrations,[74] the results being given in Table V.

TABLE V. - DENSITIES OF AQUEOUS SODIUM IODIDE SOLUTIONS

Molal concn.	Density
0·04404	1·002093
0·06937	1·004972
0·08846	1·007132
0·12445	1·011209
0·15104	1·014197
0·19769	1·019442
0·20309	1·020056

The apparent molal volume, ϕ, and the partial molal volume, $\bar{V}$, can be calculated from the equations:-[74]

$$\phi_{\mathrm{NaI}} = 35{\cdot}57 + 0{\cdot}80m^{1/2}$$
$$\bar{V} = 35{\cdot}37 + 1{\cdot}20m^{1/2}$$

The density of aqueous solutions at 25°C. is given by the equation:-

$$D = 0{\cdot}99707 + 0{\cdot}1118\mathrm{N.} + 0{\cdot}036\mathrm{N.}^{3/2}$$

where N. is the normality, with a maximum deviation of 0·036% between the concentration limits 0·17050 and 0·00070431N.[75]

The density of saturated solutions at different temperatures[58] is given in Table VI. The transition point of the dihydrate occurs at 68·1°C.

The densities at 54°C. of solutions in methanol are, at the respective molal concentrations;[76] 0·2753M. 0·81811, 0·1306M. 0·80198, 0·08303M. 0·79664, 0·03870M. 0·79195. The densities, measured at 25°C., of various saturated organic solutions are reported as: ethanol 1·037,[64] methanol 1·266,[63] acetonitrile 0·961,[63] and formic acid 1·668.[63] The densities and viscosities of solutions in *N*-methylacetamide have been measured over the concentration range 5×10^{-4} to 2M. and over the temperature range 30° to 60° C.[77]

TABLE VI.- DENSITY OF SATURATED AQUEOUS SOLUTIONS OF SODIUM IODIDE

Temp. °C.	Density
0·00	1·8612
35·00	1·9512
50·02	2·0169
63·10	2·1068
67·93	2·1553
70·87	2·1577
75·40	2·1544
92·23	2·1425

The variation of density with temperature for fused sodium iodide is linear and may be expressed by:-[78]

$$\rho = 3{\cdot}412 - 10 \times 10^{-4}t$$

The relative viscosity η/η_0 of aqueous solutions of sodium iodide at 25°C. is given by the following figures at the stated molar concentrations,[45] 0·290M. 1·008, 0·607M. 1·015, 1·050M. 1·032, 2·059M. 1·094, 2·947M. 1·201.

The viscosity of anhydrous methanol solutions at 54°C. is given in Table VII which also shows the viscosity increment,[76] $K = (\eta\text{soln.} - \eta\text{alc.})/\eta\text{alc.}$

TABLE VII.- VISCOSITY OF SOLUTIONS OF SODIUM IODIDE IN METHANOL

Molal concn.	Viscosity abs. units	Viscosity increment
0·2753	0·00629	0·5595
0·1306	0·005875	0·6042
0·083033	0·00573	0·622

The relative viscosity of ethanol solutions of sodium iodide at 25°C. has also been measured,[79] the values ranging from 1·00146 in 0·0007 molar solution to 1·02079 in 0·0168 molar solution. The quantity $(\eta - 1)/c^{-\frac{1}{2}}$ plotted against $C^{\frac{1}{2}}$ gives a straight line of slope 1·15 and intercept 0·027 from which η can be evaluated.

The variation of the viscosity relative to water with temperature in *n*-propanol has also been studied over the temperature range 45–55° C.[80]

The vapour pressures (±0·5 mm.Hg) from 10° to 100°C. have been measured for the systems $NaI,2H_2O$–NaI–H_2O vap., $NaI,2H_2O$–satd. solution–H_2O vap., NaI–satd. solution–H_2O vap. The following equation, derived by the method of least squares, fits all the data closely: $\log p = (-2915{\cdot}90/T) + 10{\cdot}2223$. The transition point of the dihydrate was thus determined as 68·08°C.[81] The vapour pressures of acetone solutions have been measured by the air-bubbling method from 10–50°C. and the results compared with values calculated by means of Raoult's law. The agreement is fairly satisfactory. The observed value of the molecular depression of the transition temperature to anhydrous salt (25·5°C.) was 24·0, as compared with calculated values from vapour pressure curves 26·1, and from solubility 32·8.[62] The linear variation of the Raoult coefficient with concentration has been verified for aqueous solutions of sodium iodide at 100°C.[82] Exact ebullioscopic data for sodium iodide solutions gave exactly the same constant as other alkali halides, indicating that all solutions are equally ionized.[83] The value of *K* in the Jablczynski-Wisniewski dilution law, however, increased with concentration, suggesting some association of molecules. Sodium iodide differed in this respect from all other salts tested.[84]

The conductivities of fused sodium iodide and also of fused mixtures of sodium iodide and potassium chloride have been measured. The conductivity of the pure salt can be expressed by the relation:-

$$K = 7{\cdot}35\ \mathrm{exp.}\left(-\frac{2{\cdot}130}{RT}\right)$$

where R is in g.-cal./mol.[78]

Determinations of the limiting conductivity at infinite dilution in a variety of solvents are collected in Table VIII. Unless otherwise stated, the data refer to 25°C.

TABLE VIII. - CONDUCTIVITY OF SOLUTIONS OF SODIUM IODIDE IN VARIOUS SOLVENTS

Solvent	Λ_∞	Reference
Water	126·85	75
Methanol	111·8	85
	110·3	86
Ethanol	50·0	85
	47·8	86
Acetone	184·8	87
Methyl ethyl ketone	139·0	88
Amyl alcohol	11·059	89
Hydrazine	114·5	90
Hydrogen cyanide	344·9 (18°C.)	91
Ethylenediamine	61·4	92
Acetamide	42·0 (90°C.)	93
N-Methylacetamide	17·8 (30°C.)	94
Ethyl cyanoacetate	23·40	95
o-Tolunitrile	38·05	95
Dimethylformamide	81·9	96
Furfural	40·7	97
Acetophenone	38·22	98
Pyridine	75·2	99
Benzonitrile	48·11	100
Phenol	4·88(50°C.)	101(10^{-4}M.)

The limiting conductivity has been measured in mixtures of pyridine and water from 100 to 0 mol.-% of pyridine[102] at a concentration of sodium iodide of 0·0297N. Specific conductivity curves have been determined for saturated solutions of iodine in aqueous solutions of sodium iodide (0·21 to 64·86% of salt saturation) and for various concentrations of iodine in saturated sodium iodide solution. The curve for saturated iodine in aqueous salt solutions shows a maximum at 50·09% salt saturation.[103]

The conductivity in water[75] obeys the Onsager equation up to about 0·002N.:-

$$\Lambda_\infty = 126{\cdot}90(1 - 0{\cdot}228c^{1/2}) - 59{\cdot}91c^{1/2}$$

and the Shedlovsky[104] modification up to 0·04N., the Shedlovsky coefficients being $A = 88{\cdot}84$, $B = 119$, $\Lambda_\infty = 126{\cdot}90$. The limiting equivalent conductivity of the iodide ion is 70·75 ohms^{-1} ± 0·05%.[75] The variation of conductivity with concentration in acetone[87] is very great, Λ^{25}_{100} being 1:14, as against only 1:1·8 in water and 1:1·7 in ethanol. The conductivity at 0°C. is 145·0, at 25°C. 184·8, and at 50°C. 227·5. The Kohlrausch-Debye-Hückel square root law holds for high dilutions:-

$$\Lambda = \Lambda_\infty - aC^{1/2},$$

where a is 5·19 at 0°C., 5·31 at 25°C. and 5·37 at 50°C. Stokes's law was verified, $\Lambda_\infty \eta$ being 0·575, 0·582 and 0·581 at 0°, 25° and 50°C.[87] The square root law has been found to hold well in a number of solvents, and this equation can be used to calculate conductivities at other concentrations. In liquid hydrocyanic acid at 18°C. $\Lambda = 344{\cdot}9 - 265{\cdot}0C^{1/2}$ with an accuracy of 8–10 per cent.[91] In anhydrous hydrazine at 25°C., $\Lambda = 114{\cdot}5 - 140C^{1/2}$ over the concentration range $1{\cdot}366 \times 10^{-3}$ to $2{\cdot}282 \times 10^{-2}$ molar.[90] In benzonitrile at 25°C., $\Lambda = 48{\cdot}11 + 210C^{1/2}$ holds up to 0·001N.[100] In ethyl cyanoacetate the deviation from the square root equation is 39% and in *o*-tolunitrile 73%.[95] The deviation curve $\Lambda_0' - \Lambda_0$, obtainable from an extended Onsager equation, is said to be linear with positive slope.[105]

Sodium iodide has a very low conductivity in phenol and it is suggested that this is due to feeble ionization.[101]

The specific conductivity in liquid iodine at 130°C. reaches a maximum at a concentration of $3{\cdot}7 \times 10^{-4}$ molar and decreases from $\Lambda = 2{\cdot}202$ at 0·005 molar to 0·059 at 0·327 molar. The temperature coefficient varies with the concentration of salt but is negative. This behaviour is attributed to polymerization and dissociation of polyiodides.[106] An increase in conductivity on adding iodine to amyl alcohol or acetone solutions of sodium iodide is explained similarly.[107] High temperature coefficients are found in *N*-methylacetamide, Λ_∞ being 17·8, 22·8, 28·0 and 34·0 at 30°, 40°, 50° and 60°C. respectively,[94] and in benzonitrile,[100] Λ_∞ being 30·45 at 0°C. and 68·28 at 50°C.

The equivalent conductivity–temperature curves at any given concentration in acetone show a maximum at a high temperature. Thus, at a concentration of 0·002016N. the conductivity rises from 144 at 25°C. to 190·9 at 110°C. and then decreases to 68·5 at 218°C. The temperature of maximum conductivity varies with concentration. It is concluded that this behaviour is due to changes in the dielectric constant of the solvent.[108] The effect of pressure from 1 to 10,000 kg.cm.$^{-2}$ on the equivalent conductivity has been studied with 0·01N. aqueous solution. The conductivity passes through a maximum which cannot be entirely explained by a change in the degree of dissociation of the ions. Calculation suggests that there must be a large change in the diameter of the ions with pressure.[109] An expression, derived from fundamental principles, for the equivalent conductivity in any solvent gives calculated values agreeing closely with experimental values for sodium iodide in methanol.[110]

When water or alcohol is added to a mixture of salt and dioxan in a conductivity cell, a sharp rise in current occurs at a critical concentration of the polar liquid. This effect is believed to be due to the inception of dissociation of the salt. For sodium iodide the critical concentration is[111] water 1·84, alcohol 4·4 mol.l.$^{-1}$

Independent migration of ions has been verified in methanol,[85] ethanol,[85] acetone,[87,88] methyl ethyl ketone,[88] hydrogen cyanide[91] and dimethylformamide.[96] The ionic conductivities (mobilities) and transport numbers obtained in a variety of solvents are collected in Table IX.

In contrast to the behaviour of lithium halides, it is found that adding methanol to acetone solutions has no effect on the transport numbers of sodium iodide; it is concluded that sodium iodide forms no complexes in acetone.[116]

From electrical conductivity data from solutions of sodium iodide in fused silver bromide, the ionic radii have been calculated as Na^+ 0·98A., I 2·20A.[117,118] The radii calculated from the specific volumes of solutions are somewhat greater, Na^+ 1·04A., I^- 2·51A., but smaller than those found in dilute solutions.[119] From conductivity measurements in benzonitrile the radii have been estimated

TABLE IX.- IONIC CONDUCTIVITIES AND TRANSPORT NUMBERS FOR SODIUM IODIDE IN VARIOUS SOLVENTS

Solvent	Ionic conductivity		Transport number anion	Ref.
	λ_{Na}	λ_I		
Water	44·140	65·464	-	112
Water	-	-	0·472	113
Methanol	49·4	62·7	-	85
Ethanol	21·8	28·5	-	85
Ethanol	-	-	0·582	114
Ethanol	-	-	0·5815	115
Acetone	68·6	115·9	0·628	87
Acetone	-	-	0·614	116
Methyl ethyl ketone	56	83·4	-	88
Hydrogen cyanide	132·4	212·5	-	91
Pyridine	26·8	48·4	—	99

as Na$^+$ 0·80A., I$^-$ 1·79A.,[22] and the mean radius of the cation as 2·88A. using ionic mobilities and Stokes's Law, or 3·72A. from the Debye-Hückel theory.[100] Calculations of the harmonic mean of ionic radii according to the Debye-Hückel equation and to Stokes's Law have been made from conductivity data in fourteen organic solvents. There is a rough correspondence between the two sets of results, the Debye-Hückel values being 1·05 to 7 times as great as those calculated from Stokes's Law. The discrepancies are most probably due to incomplete dissociation of the salt but may possibly be due to inadequacy of the theory.[120] The distance of closest approach has been calculated by a number of independent methods; from conductivity data 3·5A., from ionic mobilities 3·02A., and from the ionic radii 3·11A.[121] The distance between the centres of ions in solutions at the limit of full solvation has been calculated from the density of solutions as 7·70A. and from models of solutions as 7·16A.[122]

The effective radii of the hydration envelopes has been estimated as Na$^+$ 1·57.A., and I$^-$ 2·09A.[21] Co-ordination numbers of water molecules surrounding ions have been estimated from values of the ionic radii and the radius of a water molecule as Na$^+$ 6, I$^-$ 8. Agreement between calculated and experimental heats of interaction between the ions and water suggest that in this hydration envelope water molecules are in the liquid rather than in the frozen state.[21] Calculations from electrolytic water transfer in aqueous solutions indicate that the hydration numbers of sodium and iodine ions are, respectively, in N. solution 8 and 2·55, and in 0·1N. solution 7·33 and 2·0.[113] Vapour pressure data yield much the same type of results, hydration numbers 8 + 2 indicating that between 15·7 and 30·1 molecules of water are bound per ion pair in 2N. and 10N. solution respectively.[123] By making the assumption that, at the minimum observed in dielectric constant–concentration curves, all the water is bound by the ions, it is estimated that 200 moles of water are bound per mole of salt which is equivalent to 15,000 water molecules per unit ionic charge. The ion sheaths are pictured as formed of weakly bound oriented water dipoles arranged in chains round the ion.[31] The hydration of ions in 0·5M. sodium iodide is found to correspond to $NaI,14{\cdot}5H_2O$, the hydration of the sodium ion at this concentration being 11·1 and that of the iodide ion 3·4.[124] The volume of the water of hydration has been measured with an ultrasonic interferometer.[125] The solvation numbers calculated from conductivity measurement are: in acetone, sodium 4–5, iodine 0–1 and in methyl ethyl ketone, sodium 3, iodine 0–1.[88] In furfural, solvation is found to be of the same order of magnitude as in water.[97] Studies of the boiling point elevation of acetone solutions of anhydrous salt and hydrate led to the conclusion, however, that definite ionic hydrates do not exist.[126] Quantitative studies of electro-osmosis using a Pyrex glass membrane indicate that each ion maintains its own characteristic hydration number.[127]

Activity coefficients in aqueous solution have been calculated from conductivity measurements,[128,129] and from solutions isopiestic with potassium chloride solutions.[130] The values from both methods, which agree closely, are given in Table X.

TABLE X. - ACTIVITY COEFFICIENTS FOR AQUEOUS SOLUTIONS OF SODIUM IODIDE

Molar concn.	Activity coefficient	
	Ref. 128,129	Ref. 130
0·03	0·861	-
0·10	0·788	0·785
0·20	0·754	0·749
0·30	0·746	-
0·50	0·721	0·723
1·00	0·734	0·736

E.m.f. measurements in cells containing sodium iodide in ethanol without liquid junction over the concentration range 0·002–0·1N. indicate much higher values for activity coefficients than are predicted on the Debye theory. Over the range 0·01–0·1N. activities can be calculated from the equation:-[114]

$$-\log_{10}f = 1{\cdot}63C^{\frac{1}{2}} - 2C$$

The activity coefficient of sodium iodide in ethanol solutions containing both sodium and potassium iodides depends on the concentration of potassium iodide and not only on the total concentration of the mixture as required by Lewis' ionic strength principle.[131] The activity coefficient of piperidine has been found to be zero in sodium iodide solution.[132]

The equivalent refractivity for the sodium D line at infinite dilution has been determined as 19·38. The equivalent refractivity of the ions is R_{Na} 0·200, R_{I} 19·18 ± 0·03.[133] An interferometric method has been used to measure the refractive index in aqueous solutions of sodium iodide from 0·002 to 0·0002N. The difference, δn, between solution and pure solvent is a linear function of concentration,[134] the values being given in Table XI.

TABLE XI. - REFRACTIVITY OF AQUEOUS SODIUM IODIDE

Concn., N.	0·0002	0·0004	0·006	0·001	0·002
$\delta n \times 10^6$.	4·5	9·0	13·9	22·5	40·91
Refractivity function, ψ	12·7	12·7	12·7	12·66	11·47

The increments of refractive index for 1% increase in concentration have been found to vary from 0·00152 at 4·99% to 0·00146 at 19·69%.[135] The rotatory dispersion of gelatin at 40°C. in sodium iodide solutions has been found to obey a simple Drude equation[136] the numerator K of which is given by:-

$$K_{40} = 44{\cdot}5170 - 6{\cdot}220C_{\mathrm{NaI}}$$

The equivalent dispersion of sodium iodide solutions to ultra-violet light was found to decrease with increasing concentrations.[137]

The molecular light scattering of solutions of sodium iodide has been measured over a range of concentrations. Agreement between the experimental

Rayleigh constant and that derived from Debye's equation was exact, both methods giving 0·95.[138,139]

The molecular magnetic rotativity, dispersivity and refractivity together have been determined for sodium iodide solutions at various concentrations. The corresponding magneto-optic anomaly is much smaller than the theoretical value of unity.[140]

TABLE XII. - MOLECULAR MAGNETIC ROTATIVITY OF SODIUM IODIDE

Molar concn.	Mol. mag. rotativity	Mol. dispersivity	Mol. refraction	Mag. opt. anomaly
1	45·5	94·15	19·88	0·87
3	43·5	92·10	19·64	0·85
4	42·0	91·20	19·52	0·84

The absorption of ultra-violet light by sodium iodide solutions has been examined down to 1860A. In aqueous solution there are maxima at 2250 and 1920A. and a minimum at 2090A. In ethanol solution the first maximum is shifted to 2160A. and the minimum to 2040A.[141] Absorption lines different from those of the nuclear quadrupole resonance have been found in the frequency range 150–350 Mc.sec.$^{-1}$ The absorption is believed to depend on crystal imperfection and occurs in a very narrow region of the crystal.[142] Coloration has been produced in sodium iodide crystals by exposure to intense *X*-rays for 5 hours.[143] Absorption of light by *F* centres in sodium iodide crystals has been studied theoretically taking into account the vibrational excitation of the ions. Calculated values of the energy of thermal dissociation of *F* centres and of the half-width of the *F* absorption band agree reasonably well with experimental values.[144,145] *V* centres have been introduced into sodium iodide crystals by heating the crystals in the presence of iodine. These centres were, however, unstable, tending to bleach during the cooling period.[146]

The photoelectric effect has been observed by Millikan's method of exposing to ultra-violet radiation particles suspended between condenser plates.[147] The limit of the exciting radiation lies between 2170 and 2062A. with a mean of 2116A.[148] A maximum occurs in the inner photoelectric effect at 2300A.[149] A number of investigations has been made of the photodissociation of sodium iodide. It was found that the vapour at 450–600°C. at a pressure of 10^{-3} to 10^{-1} mm.Hg could be excited by radiation of $\lambda < 2500$A. to emit the sodium D lines and in some cases the lines 3302 and 3303A.[150] This could be due either to optical dissociation or to ionization of traces of sodium vapour already present. The dissociation theory was verified by the fact that the line 3303A. appeared only on irradiation with an energy corresponding to the dissociation energy of sodium iodide plus the excitation energy of the sodium atom to the 3P state.[151] The dissociation occurs in an excited sodium atom and a normal iodine atom.[152] With shorter wave-lengths the excess energy over that required to accomplish the dissociation appears as kinetic energy of the atoms, as is shown by the Doppler broadening of the emitted lines.[153] Measurement in two directions at right angles of the light emitted by excited sodium iodide vapour indicates that the atoms move in all directions with equal probability.[154,155] A theoretical study of the photodissociation suggests[156,157] that the probability of recombination of the atoms is 10^{-4} to 10^{-8}.

Sodium iodide used as a flux changes the yellow phosphorescence of zinc sulphide to blue.[158]

When sodium iodide vapour was excited in a gas discharge tube the lines detected were those of Na, I and NaI, the intensity of the sodium line being only one third that of iodine. The lines of the sodium iodide discharge were one hundred times as intense as those of pure sodium vapour.[159] The negative sodium and iodine ions produced by a discharge in sodium iodide vapour could be separated by means of a magnetic field and collected. Helium or argon caused the negative sodium ions to break up into positive ions and electrons.[160]

A number of phase rule studies of systems containing sodium iodide have been recorded. Data have been given for the construction of the boiling point, freezing point and pentahydrate solubility curves of the system NaI-H_2O. There is a eutectic at -31·5°C. and 47·1% of sodium iodide. The pentahydrate–dihydrate transition temperature is -12·3°C. when the solution contains 60·2% of sodium iodide, while the dihydrate-anhydrous salt transition temperature lies at 68·0°C. and 74·8% of sodium iodide. The boiling points of solutions range from 104·8°C. for 37·2% salt to 142·8°C. for 76·2%.[161] Vapour pressure curves have been obtained from 10° to 100°C. for the systems $NaI,2H_2O$-NaI-H_2O vapour, $NaI,2H_2O$-satd. soln.-H_2O vapour, NaI-satd. soln.-H_2O vapour.[81] A study of the system NaI–I_2–H_2O at 0°C. revealed the existence of the compounds $NaI_4,2H_2O$ and possibly $NaI_2,3H_2O$.[162] Solubility measurements for the system $NaCl$-NaI-H_2O at 10°, 25°, 50°, 75° and 100°C. showed the existence of neither double salts nor solid solutions, the only solid phases being $NaCl$, NaI and $NaI,2H_2O$.[163] Similarly, no compound formation was detected in the system NaI-KI-H_2O at 8°, 25° and 40°C. although the system $NaIO_3$-NaI-H_2O at the same temperatures showed a series of solid solutions of composition $(NaIO_3,5H_2O)_n(NaI,2H_2O)_m$, beginning with the 1:1 ratio and extending to $n = 1$, $m = 2$.[164] No double salts or solid solutions were found in the system NaI-Na_2SO_4,H_2O at 15°, 25° and 45°C.[165] Vapour pressure curves from -16° to +40°C. have been measured for two fixed systems of NaI-NH_3-H_2O.[166]

The system NaI-$CH_3{\cdot}COCH_3$-H_2O was studied between -34° and 59·8°C. and one compound, $NaI,3CH_3COCH_3$, was found to be formed, stable below 25·7°C.[167] Measurements have also been made of the solubility and vapour pressure of acetone solutions and of the lowering of the transition point of the compound $NaI,3CH_3COCH_3$ by foreign substances. The observed molecular depression of the transition point was 24·0, that calculated from vapour pressure data 26·1, and from solubility data 32·8. It is claimed that the system can be used for the accurate determination of molecular weights.[168,169] Similar measurements have been made on the system NaI–$MeOH$ which forms the compound $NaI,3MeOH$, transition point 26·4°C. The molecular depression referred to 100g. of methanol was 20·0 for polar and 18·3 for non-polar substances.[170] Dissociation pressures of this compound have been determined at various temperatures.[60]

The system NaI–KI–furfural forms no compound, and analytical data have been obtained for the six ternary points at each temperature 20°, 30° and 40°C.[171] Ebullioscopic measurements on the system NaI–carbon disulphide-methanol give results differing greatly from the values calculated by the mixture rule. Total and partial vapour pressures of the mixtures were measured and compared with values calculated by means of an extension of Nernst's theory of boiling of mixed solvents. The effect of the solute is regarded as a 'salting out' effect.[172] Conductivity, ebullioscopic and electrolysis studies have been made on the system $AlBr_3$–NaI–ethyl bromide at 18°C. and the results suggest the possible formation of complexes such as $nAlBr_3,mNaI$ and Al_2Br_6,NaI,C_2H_5Br.[173] Freezing point data for this system between 96° and 200°C. also seem to indicate the presence of a 1:1 addition compound, but sublimation studies show that exchange of halogen occurs and the solution behaves like a non-ideal mixture of $AlBr_3$ and AlI_3 with the sodium halides.[174]

The melting-point curve of the binary system KI-NaI has been determined and the depression of the melting point correlated with the lattice parameters of the components.[175] The vapour pressures of the salt pairs NaI-KI and NaI-KCl have been measured at 1180° C.[176,177] The system NaI-KI was found to give a continuous series of solid solutions, but the system (Na,K)(Cl,I) was irreversibly reciprocal, the system reacting towards KI + NaCl. There are three fields of crystallization, one of NaI-KI solid solutions, and two associated with NaCl and KCl, respectively; a multiple eutectic occurs at 504° C., with NaCl 37%, KI 46·5% and KCl 16·5%.[178] The reciprocal system (Na, K)(I, F) is also irreversibly reciprocal, the preferred phases being KI and NaF. Owing to the stability of NaI-KI solid solutions, the liquidus surface comprises only three fields, viz. (Na,K)I, NaF and KF, converging in a ternary eutectic point at 542°. The minimum on the curve of mutual crystallization of (Na,K)I and NaF is at 560° C.[179] The system $2NaI$-Na_2CO_3 has a continuous series of solid solutions, but in the system $2NaI + K_2CO_3 \rightleftharpoons 2KI + Na_2CO_3$ equilibrium is shifted to the right in conformity with the thermal value of the reaction, 4·9 kg.-cal.equiv.$^{-1}$.[180] The system $NaBr + KI \rightleftharpoons NaI + KBr$ has a cup-shaped crystallization surface with continuous solid solutions on all sides.[181] The system $AgNO_3 \rightleftharpoons AgI + NaNO_3$ has six fields of crystallization on either side of a ridge of maximum melting point 554° C. and has four eutectics; the heat of reaction is high, 28·38 kg.-cal.[182] The monotectic temperature of the system Na-NaI is 656° C. and the consolute temperature 1110° ± 50° C. The heat of solution of sodium iodide in liquid sodium is calculated as 28 ± 2 kg.-cal. mol.$^{-1}$.[183] The system HgI_2-NaI has a eutectic at 216° C. with 26 mole% of NaI and a transition point at 256° C. above which the solid is HgI_2. Addition of sodium iodide up to 11 mole% lowers the transition point from the yellow to the red modification which suggests that a chemical compound is formed.[184]

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Chemical Reactions of Sodium Iodide

In ethanol and especially in acetone solution sodium iodide reacts in the cold with ethylene dibromide or ethylene dichloride. The products are ethylene and iodine, no acetylene being formed.[1] The following mechanism has been proposed for the thermal decomposition of sodium iodide by sodium metaphosphate

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at 200–400°C.:-

$$\begin{aligned} 2NaI + Na_2P_2O_6 + \tfrac{1}{2}O_2 &\rightarrow Na_4P_2O_7 + I_2 \\ 2NaI + Na_4P_2O_7 + \tfrac{1}{2}O_2 &\rightarrow 2Na_3PO_4 + I_2 \\ 2Na_3PO_4 + Na_2P_2O_6 &\rightarrow 2Na_4P_2O_7 \end{aligned}$$

The rate of reaction depends on the shape and material of the reaction vessel, silica acting as a catalyst. The reaction has been suggested as the basis of a rapid laboratory method for the production of iodine without using concentrated sulphuric acid.[2]

The law of mass action has been verified for the equilibrium in the reaction:-

$$Na + KI \rightleftharpoons NaI + K$$

K at 800°C. being 56.[3] Mixtures of potassium chloride and sodium iodide have been studied by *X*-ray spectrography at temperatures above and below the fusion point and double decomposition has been proved to occur.[4] Equilibrium diagrams have been prepared for the systems NaOH-NaBr-NaI and NaOH-NaI.[5]

Studies have been made of the absorption velocity of sulphur dioxide by sodium iodide. Measurements of vapour pressure and of the composition of the solid phase have shown the existence of the compounds $NaI,4SO_2$ and $3NaI,8SO_2$.[6,7]

An increase in the concentration of sodium iodide produces a marked increase in the rate of solution of zinc in aqueous iodine solution. The increase is comparable with the increase in the diffusion coefficient of iodine under the same conditions and both are correlated with the decrease in the kinematic viscosity.[8]

The polyiodide equilibrium has been studied in aqueous sodium iodide solutions with and without the addition of sodium sulphate. The values of the equilibrium constant for the tri-iodide reaction are not constant but are approximately the same in the presence and absence of sulphate at similar concentrations of sodium iodide. The agreement between these values is shown to be closer than would be anticipated from the activity theory. It is concluded that polyiodides more complex than the tri-iodide are present in the more concentrated solutions.[9] The tri-iodide ion was shown by a spectrophotometric technique to be more stable in *tert.*-butanol than in water. At water concentrations higher than 50% the complex is less stable than would be predicted.[10] It is reported that sulphamic acid and sodium iodide react to form the tri-iodide which can be isolated. Sodium tri-iodide crystallizes in brown needles, stable in the solid state but very soluble in water with hydrolysis.[11] From an acetone solution of sodium iodide and iodine it is possible to isolate a pale green compound melting at 74°C., decomposing rapidly in air but stable in an atmosphere of acetone.[1] This compound probably contains acetone, but its exact composition is unknown. A phase rule study of the system $NaI\text{-}I_2\text{-}H_2O$ at 0° revealed the compounds $NaI_4,2H_2O$ and possibly $NaI_2,3H_2O$. The liquid phase compositions at the invariant points were determined.[12]

Sodium iodide has been used in precipitation chromatography of metal ions by filtering a solution of metal nitrates through a column of sodium iodide mixed with alumina or silica gel or by filtering sodium iodide through a column impregnated with metal nitrates. The iodides precipitate in zones in a definite order.[13]

When sodium iodide in water or ethanol solution is irradiated with light, iodine is liberated at frequencies less than 2700A. at which the spectrum begins.[14] When two platinum electrodes, one illuminated, are dipped into a

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sodium iodide solution the reaction:-

$$3I^- \rightarrow I_3^- + 2e$$

occurs, the illuminated electrode functioning as the anode.[15] Sodium iodide reacts with acetophenone when illuminated. The quantity of iodine liberated is independent of the concentration of sodium iodide and is dependent only on the time and intensity of the light and hence upon the quantity of acetophenone decomposed. It is suggested that light produces an acidic substance which liberates hydrogen iodide which is subsequently oxidized photochemically.[16]

Application of a potential to a concentrated solution of lead nitrate containing a trace of sodium iodide produced a bright yellow precipitate on the cathode side although no precipitate was visible in the absence of the potential.[17]

Analyses have been made of the iodine content of sodium sulphate crystallized from solutions containing different concentrations of sodium iodide and the data can be used to prepare crystals with a definite iodine content of 0–0·3893% of iodine.[18–20]

Sodium iodide has been found to form oriented overgrowths on crystals of potassium chloride,[21] sodium chloride[22] and mica[23] when deposited from solution or from the vapour phase. Calculations indicated that there would be instability in the initially deposited layer if this were uniformly strained to fit the substrate and it was concluded that the lattice was distorted.[22] Electron diffraction studies of titania vapour condensed on to sodium iodide crystals above 450°C. gave patterns that did not correspond to known crystal forms of titania and it was suggested that reaction had occured between oxide and salt.[24] The adsorption of sodium iodide on barium sulphate crystals is reversible and a unimolecular layer is formed.[25]

Sodium iodide has been studied as a catalyst for the hydrolysis of diethyl carbonate,[26] the catalytic decomposition of hydrogen peroxide[27] and the reduction of metal oxides by hydrogen.[28] It was as effective as other alkali halides in lowering the transition point of sodium sulphate[29] and caused a very considerable increase in the optical rotation of santonin dissolved in liquid ammonia.[30]

A thorough study has been made of conditions governing the precipitation of silver iodide by addition of silver nitrate to sodium iodide, including the effects of the activity of the electrolyte, concentration and speed of stirring on the formation of the precipitate and the region of stability of sols.[31,32] Although silver iodide is practically insoluble in acetone, it dissolves readily in acetone solutions of sodium iodide, three molecules of silver iodide being dissolved per molecule of sodium iodide, suggesting that a complex ion is formed.[33] Tyndallometric measurements of the process of solution of silver iodide by aqueous sodium iodide solutions show, however, that the complex ions formed in this solvent are not stoicheiometrically defined but are rather associations of ions of silver and iodine in various proportions.[34]

Electrolysis of sodium iodide in anhydrous acetic acid with silver electrodes gave silver iodide in quantitative yield.[35] The distribution of thallous ion has been determined between supernatant liquor and sodium iodide crystals slowly precipitated from saturated solution at 95°C.[36] When solutions of sodium iodide in liquid sulphur dioxide are electrolyzed, very unstable products are formed at the cathode.[37]

Sodium iodide, in common with other alkali halides, was found to retard the precipitation of calcium tartrate when the concentration of salt was greater than that of the tartrate.[38]

There have been a number of studies of the neutral salt effect including sodium iodide. The concentration of hydrogen ion of solutions 0·1N. in HCl and 0, 1, 2, 3 and 4N. in sodium iodide was 0·096, 0·192, 0·241, 0·472, 1·020. The increase in hydrogen ion concentration was much greater than in corresponding solutions of sodium chloride and bromide.[39] The measurements were made by means of a hydrogen electrode against a calomel electrode. The effect of the salt on the inversion of cane sugar and the hydrolysis of ethyl acetate has also been measured. The reaction constant increased with increasing concentration of salt and was, moreover, not constant but continued to rise as the reaction proceeded, indicating some inhibition.[39] The equilibrium of the hydrolysis of ethyl acetate rises from 3·7 with no salt present to 4·186 in 1·9N. salt, the curve being convex to the concentration axis. For this reaction, the Hofmeister series does not appear to hold for the alkali halides.[40] The dispergation of cellulose in a concentrated aqueous solution of sodium iodide has been investigated. The effect of the sodium salt lies between those of the lithium and potassium salts.[41]

Sodium iodide has been included in series of salts in investigations of the lyotropic series and the salt effect on the change of vapour pressure of a water-organic liquid system[42] the penetration of ions into surface films,[43] the mutarotation of glucose,[44] the hydrolysis of esters,[45] the flocculation of cellulose ethers,[46] the carry-over of salts with vapour,[47] the extraction of triethanolamine oleate, from aqueous solution by benzene,[48] the micelle formation in colloidal systems[49] and on the rate of lowering of surface tension of aqueous solutions by detergents.[50]

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Applications

Sodium iodide has been used as an electrolyte in aqueous ethanol for liquid-level tilting switches effective in the temperature range −65° to 80° C.[1]

Fruit can be protected against fungal attack by soaking or spraying with dilute sodium iodide solution and subsequently at intervals exposing to ozone which releases iodine.[2]

Sodium iodate and chlorate may be prepared by treating at 80°C. with chlorine dioxide an aqueous solution containing sodium iodide and caustic soda. Barium iodate is separated by adding barium hydroxide and treatment of this precipitate with sodium carbonate gives sodium iodate.[3]

The usefulness of sodium iodide as a pyelographic medium in *X*-radiography is improved by making it antiseptic by the addition of mercuric iodide.[4]

Sodium iodide crystals containing thallous ion, NaI(Tl), may be used for scintillation counting of elementary particles and γ-radiation.[5]

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Analysis

Specific gravity tables at 15°, 20° and 25°C. have been published to

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enable the concentration of sodium iodide solutions to be rapidly computed.[1]

Metallic impurities in sodium iodide solutions intended for injection may be determined by flame photometry.[2]

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Organic Reactions

Sodium iodide forms a number of addition compounds with simple organic compounds, usually of the type NaI,3X. These compounds frequently crystallize from solutions of the salt in an organic solvent and commonly have a well-defined transition point above which they are unstable. Thus, methanol forms $NaI,3CH_3OH$, stable below 26·4°C. with a heat of fusion calculated[1] as 7276 g.-cal.mol.$^{-1}$ Acetone forms the well-defined $NaI,3CH_3CO{\cdot}CH_3$, with a transition point at 25·5°C.[2] The compound is said to be so stable that heating to 160°C. for 2½ hours does not drive off all the acetone.[3] In acetone solution the complex dissociates into sodium iodide and acetone and also[3] into Na^+ and $(I, 3CH_3COCH_3)^-$. The solubility and vapour pressure have been measured over a range of temperatures.[4] From dimethylformamide white needles separate of $NaI,3H{\cdot}CO{\cdot}N(CH_3)_2$, melting at 95°C. The solubility of acetylene in acetone has been found to increase with the concentration of dissolved sodium iodide, but the same is not true with dimethylformamide as solvent. This has been interpreted as indicating greater stability of the latter complex with sodium iodide.[5] Dioxan forms the relatively stable compound $NaI, 3C_4H_8O_2$.[6]

The addition compound with methyl ethyl ketone has been used as a means of purifying the ketone.[7]

In contrast to the above series, urea forms a number of compounds in which 1, 2 or 4 molecules of urea are combined with each molecule of salt.[8] A study of the crystal structure of the complex sodium iodide–cysteylglycine showed that the unit cell contained two molecules of salt to four molecules of dipeptide. The molecules were found to exist in an extended chain bound end to end by strong hydrogen bonds, adjacent chains being held together by weaker hydrogen bonds, by ionic bonds between oxygen and sodium ions and by similar bonds between hydrogen atoms and iodide ions.[9] Complex salts formed between *N*-hydroxyphthalonimide (X), iodine and sodium iodide, had the general formula $X_{12},2NaI,I_7$.[10]

There have been many studies of the kinetics of the exchange reaction between sodium iodide and an organic iodine compound, using sodium iodide containing radioactive iodine ^{131}I. Data for the principal reactions studied are given in Table XIII, the second order rate constants being usually measured at a concentration of 0·1M.

In some cases the solvent appears to have an appreciable effect not only on the activation energy and rate constant but on the actual order of the reaction. Thus, the exchange reaction with ethyl iodide is second order in both acetonitrile and ethanol but the activation energy is 18 kg.-cal.mol.$^{-1}$ in the first solvent as against 19–21 in the second, so that the rate of exchange in acetonitrile is 20–35 times as great as in ethanol.[12] In the case of *p*-iodonitrobenzene, however, the reaction is second order in acetonitrile but first order in 2-octanol.[16] The reaction with iodobenzene is also first order in 2-octanol.[17] In the same solvent, the reaction with iodophenols is first order with respect to each reactant, but that with the iodotoluenes is first order with

TABLE XIII. - KINETICS OF EXCHANGE REACTIONS BETWEEN SODIUM IODIDE AND ORGANIC IODO-COMPOUNDS

Organic reactant	Temp. °C.	Activation energy kg.-cal.mol.$^{-1}$	Reaction order	Rate constant	Ref.
Methyl iodide	20	15·4	2nd	630×10^{-5}	11
Ethyl iodide	20	19·0	2nd	13×10^{-5}	11
Ethyl iodide	-	19–21	2nd	-	12
Propyl iodide	22·5	19·3	2nd	10×10^{-5}	11
Allyl iodide	28·5	17·4	2nd	-	13,14
*cyclo*Pentyl iodide	25	21·0	2nd	88	15
*cyclo*Hexyl iodide	25	0·844	2nd	25·6	15
*cyclo*Heptyl iodide	25	120	2nd	21·3	15
*cyclo*Octyl iodide	25	28	2nd	22·0	15
*cyclo*Pentadecyl iodide	25	9·9	2nd	20·1	15
2-Heptyl iodide	25	77	2nd	21·8	15
p-Iodonitrobenzene	240	-	2nd	1·58	16
Iodobenzene	240	-	1st	6×10^{-5}	17
o-Iodophenol	140	23·6	2nd	$13·76 \times 10^{-4}$	18
p-Iodophenol	140	23·3	2nd	-	18
o-Iodotoluene	140	38	1st	-	18
m-Iodotoluene	140	25	1st	-	18
p-Iodotoluene	140	28	1st	-	18
2-Iodonaphthalene	240	30	-	-	19

respect to the organic compound and zero order with respect to ^{131}I.[18]

Sodium iodide acts as a true catalyst in the condensation of acetaldehyde and ethanol to form acetal.[20] The kinetics of the reaction of sodium iodide with epichlorhydrin show a transition from specific oxonium ion catalysis to general acid catalysis on increasing the strength of the buffer.[21]

Attempts to prepare iodomalonic esters by treating the corresponding bromo esters with sodium iodide failed owing to coupling which resulted in the formation of tetra-carboxy derivatives.[22] The kinetics of exchange reactions with bromo- and chloro-allene,[23] and *cyclo*propyl, *cyclo*butyl, *cyclo*pentyl and *cyclo*hexyl derivatives[24] have also been investigated.

Other exchange reactions studied have included those with styrene dibromides,[25] cumene hydroperoxide,[26] tri- and tetra-chloropentanes,[27] phosphorous esters[28] and alkanephosphoric acids.[29] Sodium iodide was very active in causing the decomposition of amyl sodium.[30]

Sodium iodide reduces the sulphonyl chloride group to the corresponding sulphinate and reacts quantitatively with carbonyl chloride to give carbon monoxide and iodine, but cinnamyl and trichloroacetyl chlorides are inert.[31] A mixture of sodium iodide with dichloramine-T[32,33] or with *N*:*N*-dichloromethylcarbamate[34] has proved a useful iodinating reagent which probably acts through the intermediary of iodine chloride.

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SECTION XXXIV

SODIUM SULPHIDE

By A. B. LITTLEWOOD

Preparation and Manufacture

Sodium sulphide is manufactured in large quantities by reduction of anhydrous sodium sulphate, mainly with carbon or other solid organic material, or with hydrogen or hydrocarbon gases.

When carbon is the reducing agent, the reaction is normally carried out at 700–900°C., depending on the type of carbon and the type of furnace etc. With birch or pine charcoal, the reaction begins at 750°C., but with graphite a temperature up to 880°C. is required.[1,2] In the reaction, the carbon can be oxidized either to carbon monoxide or to carbon dioxide according to the conditions and the proportions of the reagents. If the temperature is too high, sulphur dioxide may be evolved, with the formation of sodium carbonate.[1-4] The regimens leading to this reaction, and to the formation of sulphur, have been studied *in vitro*.[5] The reaction is assisted by the use of a flux, such as sodium sulphide,[2,7-9] or the sulphide of another metal.[6,10,11] The proportions for the maximum yield are variously reported as being $Na_2SO_4:C = 4:1$,[12] $3:1$[13] or $2:1$.[14] Increase in the proportion of carbon decreases the loss of sulphur, but increases other side reactions, so that the total yield is not increased.[15] Briquetting of the charge favours the yield.[16] In modifications of the reaction, the sodium sulphate has been replaced by sodium carbonate and sulphur,[17] or by sodium chloride and sulphuric acid;[18] the carbon has been replaced by petroleum oil.[17,19] In one case both reagents have been replaced by sodium chloride and carboniferous sludge acid.[20] Many patents cover the design of furnaces and details of manufacturing processes.[21] The product is obtained by leaching with water or steam. Unchanged sulphate may be removed as barium sulphate,[22,23] or by means of lime and hydrogen sulphide.[24,25] These reagents will also remove carbonate. Addition of calcium oxide to the charge mixture also renders sulphate and carbonate insoluble.[26] The purity of the product ranges from about 50% up to 98% according to the process used.

Hydrogen, carbon monoxide, water gas or hydrocarbon gases may also be used to reduce sodium sulphate. Reaction temperatures that have been reported are 600°C. for hydrogen, 800–850°C. for natural gas,[27] 900°C. for methane,[28] 960°C. for carbon monoxide,[29] or 900°C. for producer gas.[30] With hydrogen, iron or copper together with a compound of one of the metals of periodic groups IVa, Va or VIa act as a catalyst,[23,31-35] though the reaction proceeds, but more slowly, without the catalyst. With carbon monoxide, the catalyst is required for any reaction to occur.[2] Carbon acts as a catalyst,[36] and with carbon monoxide it is a more efficient catalyst than nickel, which also may be used.[2] Sodium salts of aliphatic acids, e.g. sodium oxalate, may also catalyze the reaction.[37,38] When gases are used to reduce sodium sulphate, the reaction is slower in the liquid state than in the solid, in contrast to the case with carbon. Thus, fluxes are not used.[39,40] A number of patents apply to the process.[40]

Sodium sulphide is produced by causing hydrogen sulphide or carbon oxysulphide to react with sodium carbonate in the presence of inert or reducing gases, e.g. carbon monoxide, hydrogen, methane or nitrogen, at 400–800°C.[41-43] or by fusion of sodium carbonate and sulphur, especially in the presence of sodium hydroxide to lower the fusion temperature.[44] Sodium carbonate also reacts with sulphides, such as iron pyrites, at 800°C. to give sodium sulphides, and other products that are insoluble in water.[45,46] Sodium chromate (1 part), sulphur (2 parts) and carbon (5 parts) yield chromic oxide and sodium sulphide on heating in reducing conditions.[47]

There are several wet methods for the production and preparation of sodium sulphide, but none of these seem to be competitive with dry methods on a large scale. Sodium polysulphide may be reduced to monosulphide with sodium amalgam.[48-50] Sodium thiosulphate dissolved in concentrated sodium hydroxide solution has been reduced to sulphide under pressure at 250–300°C.[51] When sulphur is dissolved in excess of 50% sodium hydroxide solution containing a little polysulphide at its boiling point, it gives sodium sulphide among the products.[52] Barium sulphide reacts with sodium sulphate or carbonate in aqueous solution to give sodium sulphide and either barium sulphate or carbonate.[53,54]

Manufactured sodium sulphide is often discoloured brown by the presence of iron. This can be removed with sodium cyanide solution, and colourless crystals of pure sodium sulphide can be obtained from the solution.[55-57] Iron can also be coagulated to give ferric oxide either by alkali[58] and/or steam,[59-61] or by adsorption on zinc oxide.[62]

Sodium sulphide enneahydrate, $Na_2S,9H_2O$, loses most of its water easily below 100°C., but the remainder of the water (about 1 mole per mole of sulphide) is lost only with difficulty, for example in an atmosphere of hydrogen at 700°C. By carrying out the dehydration of the enneahydrate to the monohydrate at a low temperature under reduced pressure, the product never "melts in its water of crystallization", and a granular product is obtained.[63,64] The anhydrous product is sold commercially in cast shapes, in granules, or in pellets. The enneahydrate is sold as crystals.

Properties

Anhydrous sodium sulphide is a white crystalline solid, *d* 1·85 g./c.c., at 20°C.;[65] its molar volume at 0°C. is 41·5 c.c./mole.[66] It has a fluorite-type ionic lattice[67] with a lattice constant 6·526[67] or 6·52A.,[66] in which the Na–S distance is 2·83A.[66] Its melting point has been given as 1180 ± 10°C.[68] or 1200°C.,[69] both these values being higher than those previously reported.

The heat of formation from solid sulphur and sodium dissolved in liquid ammonia has been found to be −89,800 g.-cal./mole, from which the heat of formation from the solid elements at −33°C. is calculated as −87,000 g.-cal./mole.[70] The heat of formation from the solid elements at 25·0°C. has been given also as −89,200 g.-cal./mole.[71] The entropy of solid sodium sulphide at 25°C. is reported as 23·6 g.-cal./°C./mole[72] or 18·3 g.-cal./°C./mole.[73] The free energy change for the reaction:-

$$4Na\ (s,\ l,\ or\ v) + S_2\ (vapour\ at\ 1atm.) = 2Na_2S\ (s\ or\ l)$$

is given by the equations:-[72]

$$\Delta G^\circ_{298-371^\circ K.} = -208{,}000 + 56{\cdot}1T\ (Na,\ s;\ Na_2S,\ s.)$$

$$\Delta G^\circ_{371-1187^\circ K.} = -210{,}500 + 62{\cdot}9T\ (Na,\ l;\ Na_2S,\ s.)$$

$$\Delta G^\circ_{1187-1192^\circ K.} = -303{,}000 + 140{\cdot}8T\ (Na,\ v;\ Na_2S,\ s.)$$

$$\Delta G^\circ_{1192-1600^\circ K.} = -300{,}600 + 138{\cdot}8T\ (Na,\ v;\ Na_2S,\ l.)$$

The free energy of formation of either solid or liquid sodium sulphide is given by:-[71]

$$\Delta G_{298-1193^\circ K.} = -95{,}529 - 48{\cdot}87T\log T + 150{\cdot}875T$$

$$\Delta G_{1193-1600^\circ K.} = -131{,}337 - 120{\cdot}31T\log T + 400{,}684T.$$

Alternative values for the free energy of formation at 25°C., -86,500 or -86,700g.-cal./mole,[74] are approximately consistent with the above equations. It should be noted that the melting point for sodium sulphide used by the authors in producing the above figures (920 or 919°C.) is not consistent with the values reported above.

Sodium sulphide dissolves in water with the evolution of 15·6kg.-cal./mole in the formation of a dilute solution.[68] As a result, both the anhydrous salt and its hydrates are deliquescent. The solubility in water is given as a function of temperature in Table I.[75]

TABLE I. - SOLUBILITY OF SODIUM SULPHIDE IN WATER

Temp. °C.	Solubility, wt.-% of anhydrous Na_2S	Density g./c.c.
20	16·57	1·1682
30	19·80	1·1972
40	23·25	1·2287

Densities of aqueous solutions at different temperatures are given in Table II,[75] and other values are given in handbooks of chemistry. Sodium sulphide is somewhat soluble in methanol and in ethanol, in which it is reported to be less ionized than in water.[76] It is slightly soluble in benzyl alcohol, but it is insoluble in acetone, benzene or xylene.[77] Viscosities of aqueous solutions have been determined.[78,79]

TABLE II. - DENSITY OF AQUEOUS SOLUTIONS OF SODIUM SULPHIDE

Wt.-% of anhydrous Na_2S	Density at		
	20°C.	30°C.	40°C.
10	1·1014	1·0982	1·0949
12	1·1217	1·1184	1·1151
14	1·1420	1·1386	1·1352
16	1·1624	1·1588	1·1554
18		1·1790	1·1756
20			1·1958
22			1·2161

Aqueous solutions of sodium sulphide will dissolve mercuric sulphide and antimonious sulphide, which are insoluble in water.[80,81] In both cases, thiosalts are formed, and the amount of the sulphides that dissolves increases with increase in the concentration of the sodium sulphide. Sodium sulphide decreases the water solubility of sodium carbonate, and as the temperature rises, sodium carbonate becomes progressively less soluble in a saturated solution of sodium sulphide.[82]

Fused mixtures of sodium sulphide with sodium sulphate[83] and sodium carbonate[84] have been studied. With the former, there is a eutectic melting at about 730°C. with about equal weight proportions of the two components; with the latter, there is a eutectic mixture melting at about 795°C. containing 42·5% by weight of sodium sulphide. If mixtures with carbonate are heated strongly, there is a slight evolution of carbon dioxide and carbon oxysulphide, whose combined vapour pressure is about 9 mm. Hg at 940°C.[84] Sodium sulphide forms liquid mixtures with various other metallic sulphides, e.g., ferrous, cuprous, and plumbous, but zinc sulphide does not dissolve in the fused salt.[85,86] With cuprous sulphide, a compound Cu_2S,Na_2S is formed in the liquid phase with a free energy of formation of 7kg.-cal./ mole.[87]

In addition to the hydrates of sodium sulphide already described (Mellor, II, 623-4), a decahydrate is stable between 0°C. and 4·7°C.[88] Investigation of the ternary system sodium sulphide-sodium sulphate-water yields the information that there is a certain amount of mixed crystal formation, with sulphate containing up to 1·5% of sulphide, at 0·1°C.; the mixed crystal formation decreases as the temperature rises.[88] Sodium sulphate has the effect of depressing the transition point between ennea- and deca-hydrates of sodium sulphide; a saturated solution lowers it from 4·7°C. to 2·3°C. In an investigation of the hydrates of sodium sulphide, some evidence was found for a monohydrate above 85°C. The only others found were those with 9 and 5·5 molecules of water.[89]

Sodium sulphide is readily oxidized either dry or in solution. Massive sodium sulphide will burn if heated continuously in a stream of oxygen, but the flame is not self-sustaining. Powdered sodium sulphide will maintain its own combustion, but it is not spontaneously inflammable at room temperature in oxygen. The addition of drops of water to the powdered sulphide causes considerable heating, but not sufficient to cause ignition, either in air or in oxygen. The product of combustion is probably sodium sulphate. Sodium sulphide containing water, or hydrates of sodium sulphide, are not inflammable under any conditions.[90,91]

Although dry sodium sulphide is unattacked by dry air or oxygen at moderate temperatures,[68] it is rapidly oxidized in the presence of a small amount of water. At temperatures of about 160-250°C., the product is mainly sodium sulphite, with smaller quantities of thiosulphate.[92,93] At temperatures above 250°C., sodium sulphate is also formed.[92] Such oxidations have been reported as being accelerated by light.[94] During storage, sodium sulphide oxidizes in contact with air, forming largely thiosulphate and carbonate,[95] and deliquescing. Thus, commercial samples are likely to contain these contaminants. In solution, sodium sulphide is oxidized by oxygen largely to thiosulphate, small quantities of sulphite and sulphate also being formed.[96-98] The rate of reaction of sodium sulphide with oxygen is almost doubled by heavy metal catalysts such as Mn, Co, Fe or Cu.[99] Ferric hydroxide will also oxidize sodium sulphide solutions to sulphite.[100] It is reported that sodium sulphide enneahydrate changes slowly to sodium thiosulphate, sodium hydroxide, and sodium sulphate.[101] The decomposition of solutions of sodium sulphide can be inhibited to some extent by organic substances such as glycerol.[102]

Fused sodium sulphide will attack metals, including silver, gold and platinum, but it does not attack graphite.[68] Solutions of sodium sulphide will stain the surfaces of many metals, forming films of sulphide.

Sulphur dioxide reacts with sodium sulphide in solution to give largely sodium thiosulphate. The same result can be obtained by the reaction of hydrogen sulphide with sodium sulphite; the systems are the same.[103,104] This reaction, which is of commercial importance, has been studied potentiometrically[103] with a view to minimizing the loss of sulphur in side reactions. Dry sulphur dioxide and sodium sulphide give sodium sulphate and sulphur.[105]

The hydrolysis of sodium sulphide in aqueous solution has been investigated, using the solubility of mercuric sulphide as a measure of the sulphide ion concentration. Table III shows the hydrolysis of solutions of different strengths, and also the hydrolysis in sodium hydroxide solutions.[106] It is apparent that dilute solutions are almost completely hydrolyzed. A result of this hydrolysis is that sodium sulphide solutions exhibit many of the properties of the hydroxyl ions they contain. Such solutions will dissolve alumina to

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TABLE III. - PERCENTAGE HYDROLYSIS OF SODIUM SULPHIDE IN WATER AND SODIUM HYDROXIDE SOLUTION

Sodium Sulphide Concentration (M.-Na_2S)	Sodium Hydroxide Concentration (M.-NaOH)				
	0	0·25	0·50	0·75	1·5
		25°C.			
0·15	92·7%	79·7%	66·7%	56·8%	37·8%
0·25	91·9%	80·3%	–	58·7%	41·0%
0·35	83·8%	71·9%	–	55·1%	33·1%
		110°C.			
0·20	89·3%	79·3%	67·1%	51·9%	43·1%
		165°C.			
0·20	92·0%	84·5%	72·0%	53·5%	46·9%

form aluminate just as well as solutions of sodium hydroxide.[107,108] Silica will dissolve in sodium sulphide solution, but its solubility is only about half of that in sodium hydroxide solution.[109] Sodium sulphide inhibits the 'causticising reaction,' *i.e.*, the metathesis of sodium carbonate and calcium hydroxide. This effect is particularly relevant in the kraft paper industry, where it is necessary to convert sodium carbonate to sodium hydroxide in a liquor containing sodium sulphide.[110-112] Both silica and alumina will dissolve in fused sodium sulphide or fused mixtures containing sodium sulphide. Thiosilicates of the type SiO_2,nNa_2S are said to be formed.[113-115]

Carbon disulphide reacts with sodium sulphide to form sodium trithiocarbonate, Na_2CS_3. In ethanol solution, the reaction evolves 5,700g.-cal./mole.[116] The same reaction has been carried out in a solution of liquid hydrogen sulphide.[117] It cannot be carried out in aqueous solution, on account of hydrolysis. The same product is obtained by the reaction of carbon disulphide and sodium hydroxide, with sodium sulphide as an intermediate.[118] From studies of this reaction, it is concluded that the activation energy of the reaction $Na_2S + CS_2 \rightarrow Na_2CS_3$ is 12·8kg.-cal./mole.[118]

The reaction of carbon dioxide with solutions of sodium sulphide produces a complicated equilibrium system in which two weak acids are in competition. The essential equilibrium involved is that of the reaction:-

$$HS^- + H_2O + CO_2 \rightleftharpoons HCO_3^- + H_2S$$

for which the equilibrium constant is of the order of unity, and thus a mixture of carbonate and sulphide of not too large a pH will have a considerable vapour pressure of both carbon dioxide and hydrogen sulphide, unless either sulphide or carbonate is present in large excess.[119,120]

Sodium sulphide acts as an inhibitor in the solution of carbon steel[121] and copper[122] in nitric acid. The probable reason is that the oxides of nitrogen and nitrous acid are reduced by the sulphide. A number of other compounds also inhibit the reaction.

When solutions of sodium sulphide are electrolyzed with a low current density, the only product is sodium polysulphides; at a higher current density, sulphate and dithionate are formed. There is a limiting current above which sulphur is deposited on the anode. This limiting current increases with increase in the concentration of polysulphides present, reaches a maximum, and as further polysulphides form, it passes through a maximum, and eventually returns to zero. This may lead to a periodic effect in which current may alternately rise and fall as sulphur is deposited and subsequently dissolved from the electrode. The phenomenon is complicated.[123-125] The electrolysis takes place without gas formation, and thus is independent of pressure.[126]

Sodium sulphide reacts with solutions of sodium nitroprusside to give an intense blue colour which is often used as characteristic of the sulphide ion. The compound formed has been shown to have the formula $Na_4Fe(CN)_6NOS$.[127,128] Another blue compound of formula $Na_6Fe_2(CN)_8S_2$, stable in alkaline solution but rapidly decomposing at a pH below 9, has also been isolated.[129]

A standard organic reaction of sodium sulphide and sodium hydrosulphide is that in which they produce sulphides and mercaptans from halogen derivatives, or from esters such as p-toluenesulphonates.[130] In many other circumstances, sodium sulphide may be used to introduce sulphur into organic molecules.

Applications

Up to a few years ago sodium sulphide was used in very large quantities as an intermediate in the manufacture of sodium carbonate by the LeBlanc process. This is now obsolete.

An important application of sodium sulphide is its use in removing the hair from hides before they are tanned. Solutions of sodium sulphide made alkaline with either sodium hydroxide or lime are used, and it is suggested that the reaction requires the presence of the sulphide ion.[131] The rate of the reaction by which the hairs are loosened increases with pH and the sulphide concentration up to a molar concentration, but declines at concentrations greater than molar.[132] The process has been extensively reviewed[133] and discussed,[134] mainly in technological literature. In the same way, solutions of sodium sulphide will dissolve horn keratin,[135] and wool.[136,137] Though sodium hydroxide will also dissolve these materials, the action of sodium sulphide does not depend merely on the hydroxyl radicals present, but involves a specific action which results in the oxidation of the sulphide to thiosulphate, sulphite and sulphate.[136]

Sodium sulphide is an intermediate in the preparation of kraft pulp, in which wood is pulped with a solution containing sodium sulphide, sulphate, and hydroxide.[138] The mechanism by which wood lignin is decomposed by sodium sulphide has been studied.[139]

Extensive use of sodium sulphide is made in the manufacture and use of sulphur dyes.[140]

Sodium sulphide has been used in a number of metallurgical processes. It has been used as a flotation agent for sulphide and other ores.[141] A process in which lead is extracted from its sulphide by reaction with a mixture of zinc oxide and sodium sulphide has been patented.[142] A slag containing sodium sulphide has been used to remove copper from molten iron,[143] and such a slag can also remove sulphur from iron.[144] Solutions of sodium sulphide have been used to extract gold from activated charcoal containing adsorbed gold.[145] Fused sodium polysulphide has been used for descaling titanium,[146] and sodium sulphide has been used to produce corrosion-resistant films on magnesium alloys.[147]

Other reported uses of sodium sulphide include its use as a sensitizer of silver bromide sols;[148] its use in photographic toning solutions;[59,60,149] as a reducing agent in combination with glucose;[150] and in the extraction of low boiling tar-acids from tar oil.[151]

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SODIUM HYDROSULPHIDE

A number of patents describe several ways of preparing solutions of sodium hydrosulphide and its hydrates. If hydrogen sulphide is passed into a saturated solution of sodium sulphide, and sodium sulphide is continually added, a concentrated solution of the hydrosulphide is obtained. Such a solution prepared at 100°C. or 150°C. may contain up to 70% of sodium hydrosulphide. Insoluble impurities may be filtered off at this temperature, and pure sodium hydrosulphide crystallizes on cooling.[1] The hydrogen sulphide for this reaction may be obtained by the action of sodium bisulphate on another portion of sodium sulphide.[2] Hydrogen sulphide in refinery gases may be absorbed in sodium hydroxide solution to give sodium hydrosulphide solution. By using a deficit of sodium hydroxide in a counter current flow system, the formation of sodium sulphide is prevented,[3] and this also serves to prevent the adsorption of malodorous organic matter.[4] Sodium carbonate will also dissolve hydrogen sulphide to give a system containing sodium hydrosulphide. If carbon dioxide is mixed with the hydrogen sulphide before adsorption, carbonates can be removed as sodium bicarbonate or its double salts with sodium carbonate.[5] In other methods, barium sulphide reacts with either carbonates or sulphates in solution to give sodium hydrosulphide.[6] Sodium hydrosulphide solution can be made from a solution of the calcium salt by the action of sodium carbonate.[7]

In addition to the preparation given in Mellor, II, 642, the following instructions provide a quick recipe for an aqueous methanolic solution of sodium hydrosulphide:-[8] dissolve 13g. of sodium sulphide enneahydrate in water to make 100c.c., add 14g. of sodium bicarbonate with stirring, keeping the temperature of the mixture below 20°C. Add 100c.c. of methanol, still keeping the temperature below 20°C. After 30min., filter and wash the precipitate with methanol. The filtrate is a solution of sodium hydrosulphide containing little carbonate.

Solutions largely containing sodium hydrosulphide can be made by saturating solutions of sodium sulphide with hydrogen sulphide.

At room temperature, sodium hydrosulphide has a rhombohedral unit cell, of side 3·99 A., and angle 68° 5′. There is a high temperature form, stable above 90°C., having the sodium chloride lattice structure with unit cell of side 6·05A., in which the SH^- ion has spherical symmetry, and a radius of 1·99A.[9]

The constant for the reversible reaction $Na_2S(aq.) + H_2S \rightleftharpoons 2NaHS$ has been given as 0·0126 for aqueous solutions.[10]

Cyanamide and sodium hydrosulphide at about 300°C. give sodium thiocyanate in 90% yield.[11]

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SODIUM POLYSULPHIDES

Mellor, (II, 629-640) in his section on alkali polysulphides, presents a great deal of conflicting evidence from which he finds difficulty in deducing much certain information. All the work described on sodium polysulphide has been repeated (1930) by Pearson and Robinson,[1] and the few papers on the subject appearing since then conflict only slightly with their findings. What follows, therefore, draws heavily upon this paper.[1]

Three polysulphides certainly exist, sodium di-, tetra- and penta-sulphides, Na_2S_2, Na_2S_4, Na_2S_5. All these form hydrates.

Preparation

Sulphur will dissolve in solutions of sodium sulphide with formation of polysulphides. The reaction is slow, and is accelerated by using finely divided sulphur and mechanical agitation. Thus, particles of 120μ average diameter dissolve in about 9hr.[2] When the solution contains sulphur so as to give Na_2S_5, it is saturated with respect to sulphur.[2] The more sulphur there is already present in solution, the more slowly does further sulphur dissolve. Thus solutions of Na_2S_2 dissolve sulphur more rapidly than those of Na_2S_4.[3] This reaction is not suitable for preparation of sulphides, since oxidation to thiosulphate may occur, and the polysulphides are not easily crystallized from the aqueous solution.

A superior method of preparation is by the solution of calculated quantities of sulphur in aqueous alcoholic solutions of sodium sulphide.[1] Such solutions, on crystallization at −18°C. ± 2°C. (in an ice and salt bath) yield crystals of sodium disulphide for S/Na ratios from 1 to about 1·6; sodium tetrasulphide for S/Na ratios from about 1·6 to 2·6, and sodium pentasulphide for S/Na ratios greater than about 2·6. The ratio of water to ethanol does not appear to be important; mixtures containing from 10% to 30% by volume of ethanol all give satisfactory results. When the S/Na ratio is between 1·09 and 1·94, an oil separates below the main solution. This consists of a concentrated solution of sodium polysulphides whose S/Na ratio is always closer to 1·5 than that of the whole system, and from which a sodium trisulphide can be crystallized when the S/Na ratio lies between about 1·5 and 1·75. When the S/Na ratio in the oil is less, the crystals are the disulphide; when the ratio is greater, the crystals are Na_2S_4. The range of existence of oil from which Na_2S_4 can be obtained, however, is very limited.[1]

Solutions of polysulphide are also obtained by dissolving sulphur in an anhydrous ethanolic solution of sodium sulphide, and crystallizing the solution. Though all the polysulphides may thus be obtained, they cannot be crystallized so easily as from aqueous ethanol, and the method does not seem to be satisfactory as a means of preparing individual polysulphides.[1]

Solutions of polysulphides are also obtained by dissolving sulphur in an absolute ethanolic solution of hydrosulphide (see Rule and Thomas, Mellor, II, 629 *et seq.*). By using calculated quantities of sulphur, and crystallizing such solutions, pure samples of sodium disulphide and tetrasulphide are obtained,[4] though Pearson and Robinson report only sodium tetrasulphide as being formed in this way. The method is complicated by the fact that sodium hydrosulphide and sodium tetrasulphide have similar solubilities in ethanol, making crystallization difficult.[1]

Sulphur will react with sodium oxide, hydroxide or carbonate when heated, with the ultimate formation of polysulphides, *inter alia*. Such methods, however, yield a mixture which may contain thiosulphate, sulphate or sulphite, which cannot be easily separated from the polysulphide. One patent applies to the process.[5]

Polysulphides can be prepared by direct combination of the elements, but for practical purposes, the violence of the reaction needs modifying. The method of combination in which sodium reacts with a toluene solution of sulphur (Locke and Austell, Mellor, II, 633) has been used satisfactorily, and affords a specific means of preparing the trisulphide. If the reaction is carried out with S/Na ratios less than 1·5, the products contain approximately the same S/Na ratio. With initial S/Na ratios greater than 1·5, the product consists of pure trisulphide.[1,6] Fehér and Berthold[4] confirm this in general, but find that the product may contain up to 3·5 atoms of sulphur for every two of sodium.

Sulphur reacts with liquid ammonia solutions of sodium to give sodium sulphide, disulphide or tetrasulphide according to the amount of sodium. The monosulphide is insoluble, but the tetrasulphide is soluble, in liquid ammonia.[7]

The system Na_2S–S has been re-investigated by Pearson and Robinson, and in general they confirm the results of Thomas and Rule (Mellor, II, 630). Maxima corresponding to Na_2S, Na_2S_2, Na_2S_4 and Na_2S_5 are all found, but there is only uncertain evidence for Na_2S_3. In this region of the curve the results of Pearson and Robinson differ from those of Rule and Thomas.[1] Direct combination of the calculated quantity of sulphur and sodium sulphide has been used to prepare anhydrous sodium polysulphides.[8] Sodium polysulphides may also be associated with sodium sulphide prepared by the reduction of sodium sulphate,[9] especially if the sulphate contains bisulphate, or if the reduction temperature is low.

Sodium polysulphides are stabilized by the presence of alkali thiocyanate.[10]

Properties

The anhydrous sodium polysulphides are crystalline solids, the disulphide being light yellow, and the pentasulphide dark yellow or red, with the other sulphides intermediate in colour. The precise colours probably depend on the state of division and the purity.

It has been suggested that sodium polysulphides cause the yellow-red colour in glass which has been fused with carbon.[11] The polysulphides melt to give amber or red liquids, sodium disulphide, m.p. 473·4°C.; sodium tetrasulphide m.p. 284·8°C.; sodium pentasulphide 254·0°C. Sodium disulphide occurs in a low temperature form (α-Na_2S_2) and a high temperature form (β-Na_2S_2), the former turning irreversibly to the latter between 150°C. and 250°C.[4] The densities of the polysulphides at 20°C. are: α-disulphide, 2·01; β-disulphide, 2·05; trisulphide, 2·08; tetrasulphide, 2·08; pentasulphide, 2·08.[4] *X*-Ray diffraction photographs of all the sulphides have been taken, and show that whereas both disulphides, tetrasulphide and pentasulphide are true compounds possessing characteristic lattices, the trisulphide prepared by the toluene method given above gives an *X*-ray photograph which is the sum of those of the disulphide and the tetrasulphide. Thus, the trisulphide is not a unique compound.[4] This observation, together with the fact that evidence for the trisulphide in the thermal analysis of the sodium sulphide–sulphur system is very doubtful,[1] confirms doubts (Mellor, II, 633) on the existence of the trisulphide, at least as an anhydrous compound. There seems little doubt, however, that a mixture with the composition of the trisulphide is produced by reaction of sodium with excess sulphur in toluene solution.[1,4,6]

All the polysulphides form hydrates; the hydrates $Na_2S_2,6H_2O$, $Na_2S_3,8H_2O$, $Na_2S_4,9H_2O$, $Na_2S_4,11H_2O$, and $Na_2S_5,6H_2O$, are formed by crystallization from aqueous alcohol.[1] The colours of the hydrates are similar to those of the anhydrous compounds. On heating at 100° C. in a stream of hydrogen, sodium disulphide loses water to give $Na_2S_2,2H_2O$ and at 200°C. nearly all the water can be removed, though there is a little hydrolysis. Similar treatment at 100°C. of the trisulphide octahydrate gives Na_2S_3,H_2O, but considerable hydrolysis occurs when an attempt is made to remove the final water molecule. On dehydration, the tetrasulphide gives the anhydrous salt with little hydrolysis. The pentasulphide cannot be dehydrated without considerable hydrolysis.[1]

Anhydrous sodium polysulphides give a vapour pressure of sulphur when strongly heated. If the sulphur vapour is continuously removed, e.g. by a stream of hydrogen, polysulphides can be desulphurized to lower sulphides. Sodium pentasulphide is rapidly desulphurized to tetrasulphide at 440° C. Sodium tetrasulphide is desulphurized to disulphide at 640° C.[1] Sulphur may also be removed from polysulphide solutions by carbon disulphide,[12] but no quantitative data are available. Reaction of sodium with an alcoholic solution of sodium tetrasulphide gives sodium disulphide,[1] but further reduction to the monosulphide does not appear to occur. In aqueous solution sodium reduces polysulphides to sulphide (see page 983).

Solutions of sodium polysulphide hydrolyze on boiling without precipitation of sulphur. The products are sulphide and thiosulphate.[13] If such a solution is oxidized with air, sodium sulphite and sulphate may also be formed.[14] Oxidation with dilute potassium permanganate solution yields free sulphur, sulphate, and thiosulphate.[15] In liquid ammonia solution, sodium polysulphides Na_2S_x are oxidized by oxygen to give sodium thiosulphate and $x - 2$ atoms of sulphur. With the disulphide, a yield of pure thiosulphate is obtained.[16] Sodium nitrite also oxides sodium polysulphides to sodium thiosulphate, being itself reduced to ammonia. In presence of excess of alkali, excess sulphur resulting from reaction with the higher polysulphides is itself oxidized to give further thiosulphate.[17]

Solutions in liquid ammonia containing sodium polysulphide can be titrated potentiometrically.[18] The behaviour of sodium polysulphides at a dropping mercury electrode has been studied,[19] and the results suggest that the equilibrium:-

$$S_n^{--} \rightleftharpoons S_{n-1}^{--} + S$$

exists for each polysulphide in solution. By assuming that in any solution of polysulphide, all other polysulphides, monosulphide and hydrosulphide are all present in concentrations determined thermodynamically on the basis that free exchange occurs between all species, the distribution of polysulphides, sulphide and hydrosulphide in any given solution can be determined by measurement of its pH, redox potential, and total sulphur content. The results obtained support the assumption, and it is found, for example, that a solution with the composition corresponding to the trisulphide will contain NaSH, Na_2S, Na_2S_2, Na_2S_4, and Na_2S_5 as well as Na_2S_3.[20] The species which can be crystallized from a polysulphide solution containing all the polysulphide ions presumably depends in the usual way on the concentrations of the ions in relation to the solubility products of the various crystalline polysulphide hydrates. The relative concentrations of different polysulphide ions depend on the total sulphur content, conveniently expressed by the S/Na ratio.

Sodium polysulphides react with organic halides, esters, etc. to form disulphides.[21] With bifunctional organic compounds, this can lead to polymer formation.[22]

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SECTION XXXV

SODIUM SULPHATE

By G. M. DYSON

OCCURRENCE

Most continents contain large sources of sodium sulphate as minerals formed by the drying of inland seas or as 'brines' formed by concentration of natural waters in lakes not yet completely dried up. In cold winters mirabilite ($Na_2SO_4,10H_2O$)[1] deposits from some U.S.S.R. lakes e.g. the Aral sea; in warmer climates such lakes deposit thénardite (anhydrous Na_2SO_4).[2,3] At Stebnik,[4] glaserite ($K_3Na(SO_4)_2$) has been reported.

U.S.S.R. lakes rich in sodium sulphate[5] include those of W. Kazakistan (Greater and Lesser Sokryl and the Aral Seas)[6] but much astrakhanite ($Na_2Mg(SO_4)_2,4H_2O$) from the Arals contains up to 7% of sodium chloride and 5% of calcium sulphate which renders it unfit for glass-making without purification. This purification is effected by adding, to a warm 30% w./v. solution of the mineral, sodium chloride equivalent to the magnesium present; on cooling the sedimented liquor to 0–4°C. mirabilite separates in almost theoretical yield.[1] Several papers[7-18] concerning the chemistry of the Karabogaz lakes deal with their content of sodium sulphate, with which, in winter, the waters are saturated so that masses of exceptionally pure mirabilite collect on the shore with no trace of iron and $MgSO_4 + CaSO_4 < 0{\cdot}03\%$.[7,8] It is converted to anhydrous sodium sulphate[9,10] by removal to artificial lagoons where, in summer, it melts, evaporates and deposits anhydrous material. This is probably the most important Soviet source of natural sodium sulphate[11-14] and proposals have been made to establish an electrolytic soda/sulphuric acid plant there[15] using the filtered lagoon brine as raw material. Similar material of lower purity can be obtained from the Levshino brine springs[19] and from the Tambukan,[20] Ansh-Bulat[21] and Batalpashinskit lakes;[22] in the latter case a process has been evolved[23] for obtaining pure sodium sulphate decahydrate from the crude deposit.

Canadian deposits in Alberta and Saskatchewan[24-27] are extensive; one deposit at Dana showed 30 ft. depth of sodium sulphate.[28] In the U.S.A. extensive deposits of anhydrous sodium sulphate have been found in Arizona[29] and in California (San Bernardino Co.),[30] and the waters of Searles Lake contain sufficient sodium sulphate for the decahydrate to crystallize on refrigerating.[31] In Nevada exceptionally pure (97·3%) thénardite is mined overlying a deposit of the decahydrate.[32-37] There are similar deposits in Nevada,[34-36] and less pure material in Wyoming[37] and New Mexico;[38] the Santa Maria lake of N.W. Argentina[39] contains 15% of sodium sulphate. There is also much sodium sulphate in Chile,[40] but the emphasis on nitrate production has tended to cause it to be regarded as a 'waste' material. Phase diagram methods for the separation of sodium nitrate from sodium sulphate (with or without sodium chloride) have been worked out.[41]

Indian deposits of thénardite at Didwana[42-43] are exceptionally pure, and the bitterns of Lake Sambhar[44] are amenable to a process of sodium sulphate

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extraction similar to that used at Searles Lake. Deposits of thénardite occur in China.[45] Italian deposits in Sicily are analogous to the deposits at Stassfurt (cf. Mellor, II, 656) but less rich in potash.[46,47] Blue sodium sulphates (aphthitalite) have been shown to be members of a series of compounds of the system K_2SO_4:Na_2SO_4:$CuSO_4$.[48]

The industrial extraction of pure sodium sulphate from natural deposits[49] and from feldspathic minerals[50] has been the subject of patents.

Sodium sulphate microcrystals have been shown to be present in[51] and to contribute to the permanence of Los Angeles smog; such particles have been prepared artificially[52] and shown to act as condensation nuclei. Similar particles have been shown to be present in the fumes from Vesuvius.[53-55]

A detailed investigation by Kuhn[56] of the mode of formation of a large number of naturally occurring minerals containing sodium sulphate has led to a fuller understanding of the mechanism by which the deposits have been produced. Some of his results are given in Table I.

TABLE I.- SOME SODIUM SULPHATE MINERAL SYNTHESES

Reactants	Name of reactant	Temp. °C.	Products	Name of products
$3K_2SO_4$ Na_2SO_4	Arcanite Thénardite	above 1·8	$K_3Na(SO_4)_2$	Aphthitalite
$3Na_2SO_4$ $MgSO_4$	Thénardite -	above 60	$3Na_2SO_4,MgSO_4$	Vanthoffite
$Na_2SO_4,10H_2O$ $3Na_2SO_4$ $5MgSO_4$	Mirabilite Thénardite -	20·6 to 71	$Na_2SO_4,MgSO_4,4H_2O$	Bloedite
$Na_2SO_4,10H_2O$ $3Na_2SO_4$ $MgSO_4$	Mirabilite Thénardite -	60 to 131	$Na_2SO_4,MgSO_4,2.5H_2O$	Loeweite
Na_2SO_4 $CaSO_4$	Thénardite Anhydrite	40 to 110	$Na_2SO_4,CaSO_4$	Glauberite

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PRODUCTION

From natural sources

Native sodium sulphate – mirabilite $Na_2SO_4,10H_2O$ – can be purified by stacking it during its deposition[1] so that the mother-liquor drains from it, melting it by solar heat[2] and allowing the clear liquid to drain from insoluble materials. On cooling again a clean dodecahydrate is obtained in which the sodium chloride content is reduced to 0·25%. The clear liquor from the melting

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of mirabilite can be used in Belopolskii's modification of the Solvay process[3] in which it is treated with ammonium carbonate to precipitate calcium and magnesium and, after sedimentation, with excess of ammonium bicarbonate. This mixture is carbonated (with CO_2 under pressure) when sodium bicarbonate separates and is removed by filtration; refrigeration of the mother-liquor produces a mixture of sodium sulphate and ammonium bicarbonate which is recycled, and by evaporation of the final liquid, ammonium sulphate is obtained. The process is represented diagramatically in Fig. 1.

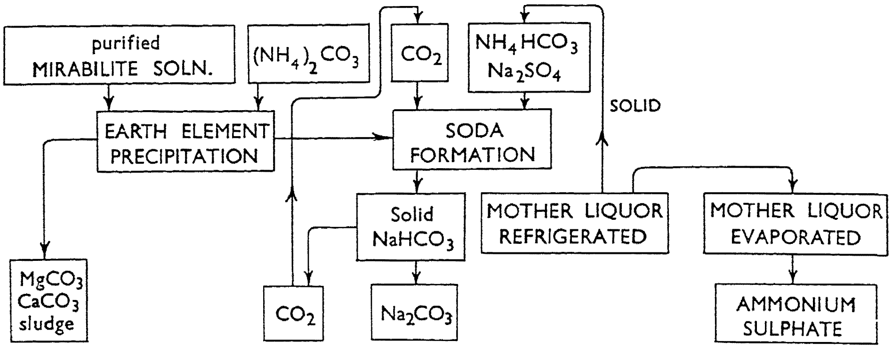

FIG. 1. PRODUCTION OF SODIUM CARBONATE AND AMMONIUM SULPHATE FROM MIRABILITE

Astrakhanite ($Na_2Mg(SO_4)_2,4H_2O$) serves as the source for much industrial sodium sulphate; it may be converted to sodium sulphate dodecahydrate and magnesium sulphate heptahydrate by heating to 25°C. with sufficient water to form a saturated solution and cooling rapidly to –2°C. to –6°C. when sodium sulphate dodecahydrate separates out and can be filtered off. The treatment of the mother liquor from such crystallization depends on the amount of sodium chloride it contains; if little, the mother liquor is evaporated to a density of 1·29–1·30 and cooled to 0° to –2°C. when epsomite crystallizes. Alternatively a mother liquor with more than 3% NaCl is treated with a magnesium chloride brine and cooled to 0°C. to precipitate epsomite.[4,5] Another method is to treat astrakhanite with just enough water to dissolve the sodium sulphate at 180°–200°C.; the magnesium sulphate remains insoluble and may be removed and the liquor worked up for sodium sulphate.[6] Yet another method[7,8] is to add sufficient sodium chloride to a hot 28% solution of astrakhanite in water to give a $NaCl:Na_2SO_4$ ratio of 3:1; on cooling to –4° to –5°C. sodium sulphate dodecahydrate crystallizes and after filtration is washed with ice-cold saturated sodium sulphate solution; a purity of 99·32% is claimed with a yield of 78%. The mother liquor is evaporated until almost all the sodium chloride has separated; this is removed by filtration and returned to the cycle leaving a mother liquor from which sulphate ion is removed by waste calcium chloride solution and the magnesium utilized as the chloride. Similar processes[9] by which astrakhanite is converted to sodium sulphate dodecahydrate and magnesium chloride hexahydrate have been investigated, using löweite ($MgSO_4,Na_2SO_4,5/2H_2O$) and vanthoffite ($MgSO_4,3Na_2SO_4$) as intermediate stages.

The crude thénardite found on the Peruvian coast has the composition:-

Na_2SO_4	56·9

NaCl	8.6
$NaHCO_3$	2.2
Insoluble matter	26.6
Water	5.7%

If this is heated to the m.p. and clarified from insoluble material, anhydrous sodium sulphate can be separated by adding salt and raising the temperature to 45°C. The resulting material is suitable for glass making.[10,11] Other natural Chilean sulphate minerals containing magnesium, zinc or aluminium sulphate can also be used to produce anhydrous sodium sulphate.[12] Kernite and zosarite,[13] which contain boric acid and sodium sulphate, are treated at 35°C. with sodium carbonate to convert the boric acid to $NaHB_4O_7$. On cooling to 15°C. most of the sodium sulphate separates as dodecahydrate and can be removed; when washed with saturated sodium sulphate solution it is almost free from boron compounds.

Sodium sulphate is also produced by a method utilising alunite, which is subjected alternately to progressively higher heat treatments and aqueous extraction; the main products are potassium alum, alumina and sodium sulphate with some potassium sulphate as a by-product.[14] This method utilises the sulphate in the mineral; raw material of a similar type less rich in sulphate needs added sulphuric acid to complete the extraction.[15]

Various methods have been devised for recovering sodium sulphate from brines and lake-waters which contain it. Brines, that are acid with boric acid and free from sodium chloride, can yield fairly pure sodium sulphate dodecahydrate after adding sodium carbonate to neutralise the boric acid and to provide carbon dioxide which prevents iron and aluminium compounds from precipitating when refrigeration is applied.[16] Brines rich in sodium chloride are treated with sufficient magnesium sulphate liquor to convert the chloride to sulphate, which is then separated by cooling and filtration. The residual liquor rich in magnesium chloride is slurried with lime, filtered and the sludge treated with very finely ground calcium sulphate (anhydrite) when the reactions:-

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$
$$Mg(OH)_2 + CaSO_4 \rightarrow Ca(OH)_2 + MgSO_4$$

take place. The lime slurry from the second reaction is used to treat a further batch of magnesium chloride liquor and the magnesium sulphate is used again in the production of a further batch of sodium sulphate.[17]

A sodium sulphate-carbonate (burkeite-$Na_2CO_3,2Na_2SO_4$) is obtained as one product of the working up of Searles Lake brine which has the approximate composition:-

KCl	4.7
NaCl	16.35
Na_2CO_3	4.7
Na_2SO_4	7.0
$Na_2B_4O_7$	1.5
Na_3PO_4	0.2

Since the brine is saturated with sodium chloride the phase relations on concentration and cooling are expressed by the three diagrams shown in Fig. 2.

The composition of the brine is shown at the point B (Fig. 2*a*) but owing to the considerable tendency of hauksite, $9Na_2SO_4,2Na_2CO_3,KCl$, to form supersaturated solutions which deposit hauksite only after several weeks the existence of this compound may be ignored and the effect of isothermal evaporation of the brine may be taken as starting from point P. During such

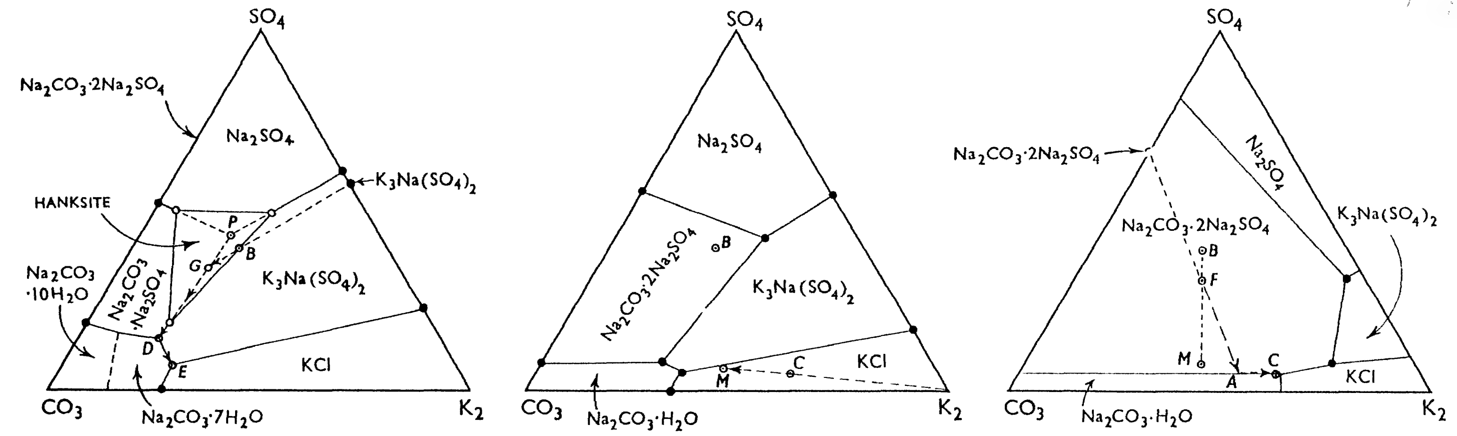
SO4
Na2CO3·2Na2SO4
Na2SO4
HANKSITE
K3Na(SO4)2
Na2CO3
·10H2O
Na2CO3
·Na2SO4
P
B
G
D
E
KCl
CO3
Na2CO3·7H2O
K2
SO4
Na2SO4
Na2CO3·2Na2SO4
B
K3Na(SO4)2
KCl
C
M
CO3
Na2CO3·H2O
K2
SO4
Na2CO3·2Na2SO4
Na2SO4
K3Na(SO4)2
Na2CO3·2Na2SO4
B
F
M
A
C
KCl
CO3
Na2CO3·H2O
K2

FIG. 2. SYSTEM Na-K-SO_4-CO_3-Cl-H_2O SATURATED WITH NaCl

(*a*) PORTION OF THE SYSTEM Na-K-SO_4-CO_3-Cl-H_2O SATURATED WITH NaCl AT 20°C. SHOWING MOLECULAR PROPORTIONS OF K_2, CO_3, AND SO_4 PRESENT IN THE LIQUID

(*b*) PORTION OF THE SYSTEM Na-K-SO_4-CO_3-Cl-H_2O SATURATED WITH NaCl AT 35°C.

(*c*) PORTION OF THE SYSTEM Na-K-SO_4-CO_3-Cl-H_2O SATURATED WITH NaCl AT 100°C.

evaporation glaserite ($K_3Na(SO_4)_2$) and sodium chloride separate until G (2*a*) is reached when burkeite begins to separate in addition to the others until D (2*a*) is reached when the solution is saturated with sodium carbonate heptahydrate. At 100°C. the picture is different (2*c*); the composition of Searles Lake brines is represented by B, but the addition of mother liquors from a previous operation brings the composition to F (M represents the composition of the mother liquor). This mixed liquor is fed to triple effect salting evaporators working on the counter current principle; two salts separate in the first two effects (at lower temperatures), sodium chloride and burkeite, until A (2*c*) is reached; during the third effect sodium carbonate separates until C is reached. The rapidly cooled liquor from the evaporator deposits potassium chloride which is centrifuged off and borax then separates from the mother liquor which is then returned to the cycle. The crude burkeite, contaminated with some sodium chloride, is used for producing sodium sulphate.[18,19] This process is virtually a large-scale development of the Dolbear process.[20] Rapid cooling of the concentrated solution of burkeite leads to deposition of sodium sulphate dodecahydrate;[21] the mother liquor can be used as a source of sodium carbonate.

Direct production of sodium sulphate from calcium sulphate by using a saturated solution of sodium carbonate in 30% aqueous sodium sulphate has been patented.[22] The increased demand for Kraft paper and detergents has made it profitable to utilize the waters of Lake Chaplin in Saskatchewan. These contain sufficient sodium sulphate to give a bed of crystals 14–24in. thick each winter.[23,24] Many similar operations are carried out on Salt Lakes; at Horseshoe Lake,[25] Saskatchewan, about 100,000–150,000 tons of sodium sulphate (95%) is extracted annually; a 98% product is obtained at the Great Salt Lake.[26]

Most of the brines are substantially $MgSO_4/NaCl$ brines in which the latter predominates; in nearly all cases the brines are naturally evaporated to obtain a salt mixture (27·6% $MgSO_4$/72·4% NaCl) which is the natural phase separating. This, when drained, redissolved in water and cooled, yields mirabilite ($Na_2SO_4,10H_2O$). 5 cu. m. of brine gives about 1000kg. of mixed salt which when dissolved in 2370kg. of water and cooled to 0°C. gives 400–500kg. of mirabilite.[27-30] The recovery is said to be improved by using several stages.[31] A similar process has been applied to the bitterns left after removing solar salt from sea-water, but the low temperature required (-23 to -30°C.) renders this process uneconomic.[32]

From chemical sources

The principal raw material for conversion to sodium sulphate is salt; the salt-cake process has been described (Mellor,II,730). Modifications in furnace design[33-35] and operating procedures[36-39] are stated to lead to a more efficient conversion of chloride to sulphate. Direct electrical heating of the acid/salt magma has been successfully used in France.[40] Attempts to replace sulphuric acid in the salt cake process have led to the Hargreaves-Robinson process in which briquettes of salt with a little clay and charcoal, and 1·7% of pyrite slag as catalyst, are heated at 500–550°C. in a stream of steam, air and sulphur dioxide. Conversion to sulphate of 96% purity is complete in 90min. and the utilization of sulphur dioxide is 40% per pass.[41-48] A development of this process is to replace the sulphur dioxide by sulphur trioxide[49,50] when the by-product gas is chlorine instead of hydrogen chloride.

There are two main processes for producing sodium sulphate *via* the carbonate or bicarbonate; in the first of these[51,52] calcium sulphate and sodium bicarbonate react under heat and pressure, with continuous evolution of carbon dioxide. The precipitated calcium carbonate is filtered off and the sodium sulphate liquor concentrated and the salt crystallized. In the second process[53] ammonia and carbon dioxide react with calcium sulphate suspended in mother liquor from a previous operation, essentially an aqueous solution of sodium sulphate and ammonium chloride. Calcium carbonate is precipitated and the residual liquor is treated with sodium chloride. Sodium sulphate and ammonium chloride can be crystallized from the liquor. By a modification of the process[54] sodium ammonium sulphate can be obtained. The use of base-exchange zeolites to convert calcium sulphate and salt to sodium sulphate has been described.[55,56]

Numerous patents cover the production of sodium sulphate by the reaction of ammonia and sulphur dioxide with sodium phosphate.[57-60] The sulphite and bisulphite first formed can be oxidized by air or by heating under pressure when the sulphate and free sulphur are formed. Mixtures of ammonium phosphate and sodium sulphate are obtained which are separated by crystallisation.

Magnesium sulphate is sometimes used as a source of sulphate ion for sodium sulphate manufacture; with brine, sodium sulphate decahydrate separates on refrigeration.[61,62]

Recovery.

Vast quantities of sodium sulphate are obtained as by-products, especially in viscose spinning, and their recovery is an important economic factor. In some cases the recovery is difficult, as in the manufacture of dichromate[63,64] where the impure material containing chromium and other heavy metals is dissolved in water, made faintly alkaline and heated to 70°C. with sodium sulphide to precipitate and flocculate the impurities as sulphides and hydroxides. Excess of sodium sulphide is oxidized by aerating the warm solution and neutrality is restored with sulphuric acid. Recovery from nitre-cake (sodium hydrogen sulphate) is effected[65,66] by roasting in a continuous tube-furnace with salt, when sodium sulphate and hydrogen chloride are formed. Alternative methods by which hydrogen chloride and nitre-cake are allowed to react[67] to produce 50% sulphuric acid and salt have not proved feasible on a large scale.

Considerable quantities of sodium sulphate are used in the viscose spinning-bath fluids and in Kraft paper manufacture; their recovery is an economic necessity, since just under a ton of sodium sulphate is used for each ton of viscose spun. The liquor contains, in addition to sodium sulphate and sulphuric acid, hemicelluloses, zinc and/or lead sulphate and small quantities of other organic materials. The zinc and lead are removed by simultaneous addition of sodium phosphate and sulphide;[68-70] filtration and vacuum concentration[71] and the addition of sulphuric acid yield a liquor which deposits crystals of $Na_2SO_4,10H_2O$ and $NaHSO_4$ on refrigeration. These, washed with a small amount of 17% sulphuric acid are ready for re-use. It is true that they yield an acid solution in water, but this is a desirable characteristic in the circumstances.[72-76] An electrolytic process[77] has been proposed for recovery of sodium sulphate from viscose bath waste, but it is doubtful whether it has been extensively used. A similar conclusion may be reached on processes designed to recover sodium sulphate from such wastes by anion-exchange resins.[78] Separation of sodium sulphate from sulphuric acid is claimed in a patented process, and the phase diagram for H_2SO_4–H_2O–Na_2SO_4 has been compiled. (See page 1013).

About 80kg. of anhydrous sodium sulphate per ton[79-81] of pulp produced appears in the flue and stack gases of paper-plants where black liquor is burned; this is recovered by cyclone and electrostatic precipitation and a pure material is then obtained by leaching and crystallization.[82-87] Among various other waste products from which sodium sulphate is recovered may be listed:-

Source	Method	Ref.
1 Iron oxide pigments	By concentration of the liquor remaining after Fe_2O_3 is precipitated from soda and iron sulphate.	88
2 Thiosulphate waste	Residues and liquors rich in $Na_2S_2O_3$ are heated with sodium bisulphate when sulphur and sodium sulphate are obtained.	89
3 Glass manufacture	High-sulphur fuels lead to recoverable quantities of sodium sulphate in glass-furnace flue dust and on the surface of the melt (Glass-gall).	90,91
4 Copper chloride manufacture	Equimolecular quantities of brine and saturated $CuSO_4,5H_2O$ solution at 50°C. are cooled to −10° to −20°C. and Na_2SO_4, $10H_2O$ removed by centrifuging.	92
5 Waste pickle liquor	Spent liquor is treated with sodium chloride which salts out an iron sodium sulphate. This on solution in water and refrigeration yields $Na_2SO_4,10H_2O$.	93
6 Working up pyrites	The residue from the chloridizing roast is leached and the solution deposits $Na_2SO_4,10H_2O$ on refrigeration.	94
7 Phenol manufacture	During alkali fusion of sodium benzenesulphonate by-product Na_2SO_4 is separated at two stages.	95
8 Tannery waste	Neutralization, evaporation to dryness and extraction	96
9 Anhydrite/alkali processes	The use of anhydrite ($CaSO_4$) with brine, NH_3 and CO_2 leads to accumulation of sodium sulphate in the mother liquors which are evaporated and refrigerated to give $Na_2SO_4,10H_2O$.	97,98

One of the most difficult problems in purifying sodium sulphate is the removal of traces of iron;[99] boiling with a slight excess of sodium carbonate is expensive and the filtration of the iron sludge difficult. Ion-exchange resins are now used for this purpose.

Dehydration and Drying.

The bulk of industrial sodium sulphate separates from cooled liquors as the decahydrate (mirabilite). The theory of dehydration with sodium chloride has been worked out[100] and it has been shown that to obtain 1kg. of anhydrous sodium sulphate from the decahydrate 238g.-cal. are required at 50°C. and 212g.-cal. at 25°C., both in the presence of NaCl; the corresponding heat of dehydration at 50°C. in the absence of NaCl is 414g.-cal. $kg.^{-1}$.

Much work has been done on dehydrating sodium sulphate decahydrate. The methods proposed are broadly divisible into groups: those in which the hydrate is melted and the melt dried by evaporation, atomising or blowing with superheated steam[101-115] and those in which the hydrate is maintained solid throughout.[116-122] In the latter the best type of drier appears to be a tower in which the crushed hydrate is fed onto an upper tray and is scraped periodically to lower trays until it emerges dry and anhydrous. The current of warm air entering the tower at 55°C. and leaving at 37°C. is maintained at such a speed that the crystals never become wetted with water of crystallization. A fuel efficiency of 40–45% is obtained.

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Some of the 'liquid' methods involve heating the decahydrate to 100°C. and seeding with anhydrous sodium sulphate, filtering off the anhydrous material and evaporating the accumulated mother liquors to obtain more anhydrous material. Considerable attention has been paid to submerged combustion for the latter purpose[123-126] and solar heat has also been used.[127,128] The use of liquid ammonia has been patented;[129] the so-called 'chemical' drying of sodium sulphate[130] is merely the production of a free-running mixture by addition of sodium carbonate. The mix is suitable for glass making.

Plant and processes have been devised for obtaining both anhydrous sodium sulphate and the decahydrate in forms suitable for further use; these are largely processes of controlled crystallization,[131-139] or special plant for separation of crystals.[140-142]

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SYSTEMS CONTAINING SODIUM SULPHATE

A very large number of systems in which sodium sulphate is one component has been examined, but very few of the phase diagrams have been determined in their entirety. In the survey which follows the reproduction of incomplete diagrams has been avoided and where possible the data are given in terms of compositions and transition temperatures.

Binary systems

System: Na_2SO_4/H_2O.

The existence of a heptahydrate of sodium sulphate is well established (Mellor,II,667) and its transition point has been accurately determined as 23·465 ± 0·004°C.;[1] replacement of H_2O by D_2O raises the transition point to 26·6–27°C.[2] The phase diagram of Na_2SO_4-H_2O is difficult to establish accurately owing to hysteresis, but the section of the diagram, Fig. 3, at the sulphate-rich end indicates that the existence of some at least of the 'polymorphic' forms of 'anhydrous' sodium sulphate (Mellor, II, 661) is confirmed.

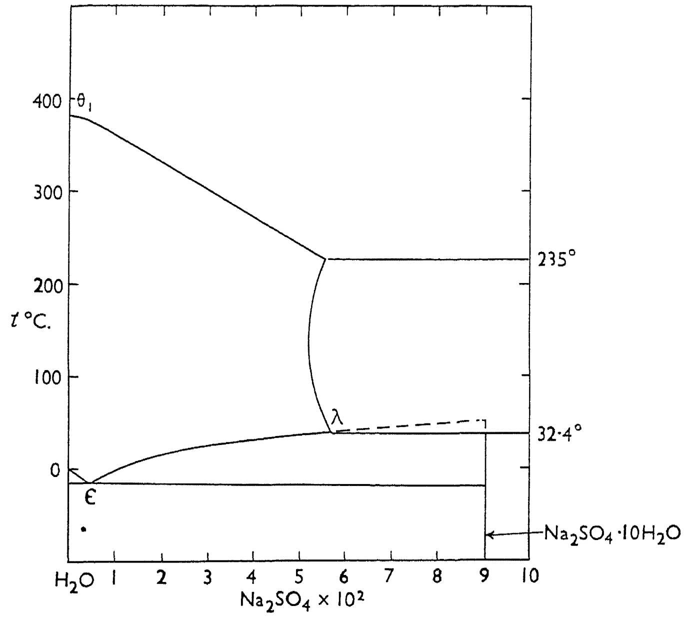


FIG. 3. SULPHATE-RICH END OF t-x PROJECTION OF Na_2SO_4-H_2O SYSTEM[3,4]

The transition point (rhombic-monoclinic) of 235°C.[4] agrees well with that given by the thermal analysis of Kracek,[5] 234·5°C. Kracek demonstrated that the breaks in the cooling curves of sodium sulphate depended on the history of the sample. Material which had never previously been heated above 125°C. gave a heating curve different from that of material which had been heated through the inversion point at least once. Kracek detected a second break in the curves between 190°C. and 234·5°C. but owing to considerable hysteresis in the inversions was unable to decide its exact position; he claims five distinct forms of Na_2SO_4, four of which are stable only in the region 190–250°C. Kracek and Ksanda[6] used *X*-ray patterns to demonstrate three forms of anhydrous sodium sulphate: (i) Na_2SO_4-I stable at 240°C.; (ii) Na_2SO_4-V stable at ordinary temperatures and (iii) Na_2SO_4-III metastable below 185°C.

Many methods have been applied to re-determinations of the transition point $Na_2SO_4,10H_2O \rightarrow Na_2SO_4$. When the vapour pressure of the change is measured it is observed[7,8] that dehydration proceeds gradually to completion without appearance of intermediate hydrates. The same is true of the heptahydrate. Rehydration at ordinary temperatures leads always to the decahydrate. Considerable discrepancies exist in the determined values of the vapour pressure of the decahydrate at various temperatures, mainly according to whether a static or dynamic method is used, the latter giving lower values. Accurate results were given by Perman and Urry,[9] confirming the isolated determinations by Schumb[10] (19·16 mm. at 25°C.) and by Wilson[11] (19·22 ± 0·02 mm. at 25°C.) and the general results of Baxter and Lansing (19·20 mm.).[12,13] The latter give

$$\log p = 10{\cdot}566 - 2794{\cdot}1\,(T+3)$$

as the equation relating absolute temperature and vapour pressure. Other workers[14] have given

$$\log p = -2710/T + 10{\cdot}37$$

as the relation, and[15,16]

$$\log p = -2837/T + 10{\cdot}7866 \text{ below } 32{\cdot}4°\text{C.}$$

with $$\log p = -2360{\cdot}58/T + 9{\cdot}2254 \text{ above } 32{\cdot}4°\text{C.}$$

The replacement of H_2O by D_2O in the decahydrate lowers the vapour pressure[2,17] (Fig. 4), and raises the transition point. The transition point of $Na_2SO_4,10D_2O$ is given as 34·48,[2] 34·5[17] and 34·6–34·9.[18]. The corresponding temperatures for $Na_2SO_4,7H_2O$ and $Na_2SO_4,7D_2O$ are 23·465°C. and 26·6–27°C.

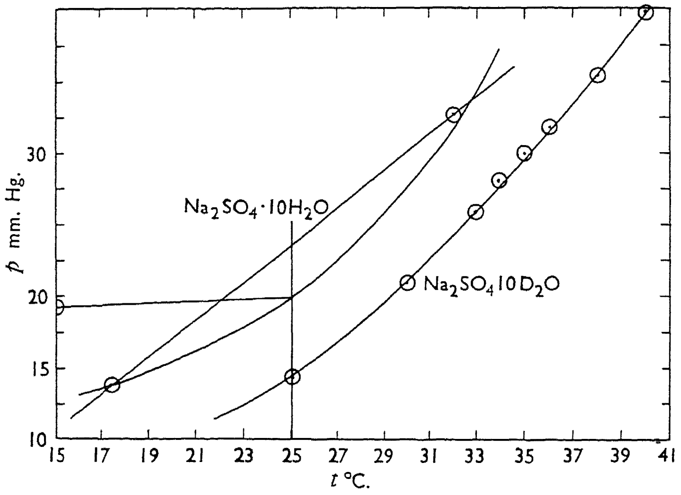


FIG. 4. LOWERING OF VAPOUR PRESSURE OF SODIUM SULPHATE DECAHYDRATE ON REPLACING H_2O BY D_2O

It has been shown[19,20] that sodium sulphate decahydrate is completely dehydrated on standing at 15°C. over 98% ethanol; in a current of dry air; in still, dry air or over 98% sulphuric acid. It is in equilibrium with and remains unchanged over 24·26% sulphuric acid at 25°C.; the vapour pressure of this solution is between that of a saturated solution of sodium sulphate and the dissociation pressure of the decahydrate.[21] If a saturated solution of the decahydrate[22] is allowed to stand over 80% sulphuric acid at 20°C. the heptahydrate crystallizes.

Among the various methods of determining the transition point of the decahydrate, Hartshorne[23] used the viscosity/temperature curves of (*a*) a solution of the anhydrous salt in water, saturated above the transition point and supersaturated below it and (*b*) a saturated solution of the decahydrate. The intersection of these curves (32·55°C.) gives the transition point (Fig. 5).

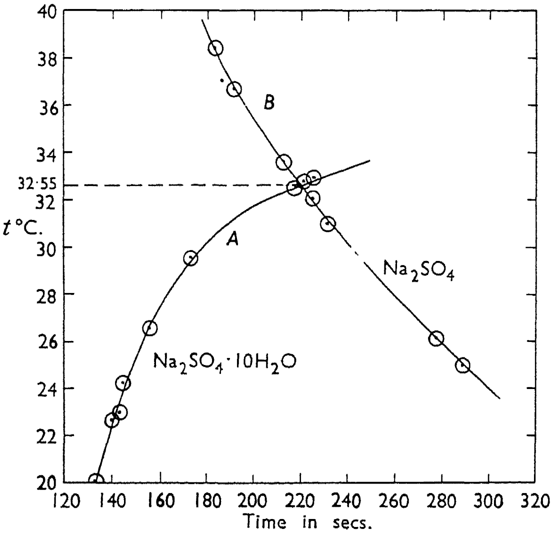


FIG. 5. VISCOSITY/t° CURVES OF Na_2SO_4 AND $Na_2SO_4,10H_2O$

Other methods used by Matsui and his co-workers were:-[24]

	Value obtained
(*a*) Dynamically by Partington's method	32·6°C.
(*b*) Cumming's dew-point method	32·6°
(*c*) Tensimeter	32·33°
(*d*) Dilatometer	32·436°

None of the results obtained appear to invalidate the value of 32·383 ± 0·001 °C. obtained by Richards and Wells and by Dickenson and Müller (Mellor, II, 667).

The transition temperature has been measured[25] by direct weighing of a crystal of decahydrate suspended in a saturated solution, the temperature of which was adjusted until the crystal neither gained nor lost in weight. The value obtained was 32·38°C. and the saturated solution at this temperature contained 49·7 g. of anhydrous salt per 100 g. of water.

The hydration of sodium sulphate has been followed by micro-wave absorption[26] (λ = 3·138 cm.); while water absorbs, neither $Na_2SO_4,10H_2O$ nor the anhydrous salt absorbs radiation of this wave-length. When the anhydrous salt is allowed to come into equilibrium with air saturated with water vapour (63% at 24–25°C.)[27] no micro-wave absorption is observed until 90% of the theoretical increase of weight for $Na_2SO_4,10H_2O$ formation has been attained. During the absorption of the last 10% microwave absorption is strong, but disappears when the decahydrate is allowed to stand. This points to the formation of saturated solutions of decahydrate on the outside of partially hydrated crystals followed by diffusion into the interior.

Fairly high temperatures are necessary for complete dehydration of sodium sulphate;[28] at 900°C. Na_2SO_4 contains 0·00002 g. H_2O per g. but on cooling, a surface film of hydrated material forms very easily.[29]

The effect of pressure on the triple point $Na_2SO_4,10H_2O-Na_2SO_4-H_2O$ is shown in Fig. 6.[30]

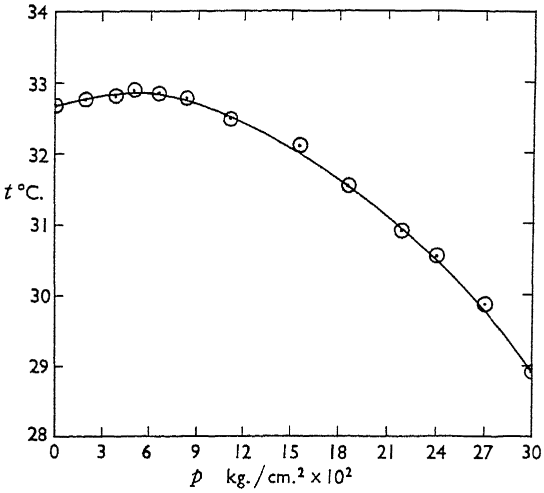


FIG. 6. EFFECT OF PRESSURE ON THE TRIPLE POINT $Na_2SO_4,10H_2O-Na_2SO_4-H_2O$

The magnetic susceptibility is unchanged as the decahydrate passes the transition point, indicating a very loose attachment between H_2O and Na_2SO_4; the decahydrate has been described as 'ice with ions'.[31] Sodium sulphate decahydrate has been proposed as a cryoscopic solvent, especially for inorganic compounds.[32,33]

A thermodynamic study of the decahydrate[34] gave the following data:- heat of formation $Na_2SO_4(s) + 10H_2O(l) = Na_2SO_4,10H_2O(s)$ $\Delta F_{298} = -1612$ g.-cal., $\Delta H_{298} = -22290$ g.-cal.; $\Delta H_{298} = -944{\cdot}3$ g.-cal.; entropy value of Na_2SO_4 at 25°C. = 35·0; theoretical heat of solution of Na_2SO_4 at 25°C. = $\Lambda_S = -19845$ g.-cal. (endothermic). Total heat of solution of $Na_2SO_4,10H_2O$ = $Ls = -17150$ (endothermic); initial heat of dilution of $Na_2SO_4,10H_2O$ at 25°C. = $\phi = 148$ g.-cal. (exothermic). Measurement of the final heat of solution of sodium sulphate decahydrate has been made calorimetrically[35] using Matignon's[36] formula $L = X_N - (\Delta + A)$, where X_N is the molecular heat of solution in a large excess of water, Δ the molecular heat of dilution and A the heat of addition. The final heat of solution was −15·525 g.-cal. per mole.

The heat of hydration of Na_2SO_4 to the decahydrate by liquid water was estimated by Merman and Urry[8] to be −20,040 to −21,500 g.-cal between 22·4°C. and 30°C. A fair agreement was obtained between these values and those calculated by the Nernst heat theorem.

When the anhydrous salt is dissolved in a mixture of water and deuterium oxide a slight but definite enrichment of the latter is found in the decahydrate which separates;[37] thus the ratio of D_2O in crystal water to that in mother liquor was 4·288:4·281.

In the industrial dehydration of sodium sulphate decahydrate to obtain the anhydrous material, direct heat has been used and internal electrical heating has been suggested;[38] cheaper methods, which also eliminate the caking troubles accompanying direct hot dehydration, are (a) chemical,[39,40] by adding boiling brine to the decahydrate in such quantity that the final temperature is 82°C.; Na_2SO_4 separates and may be centrifuged and washed free of sodium chloride by warm sodium sulphate solution and (b) physicochemical, in which the water is extracted by methanol, ethanol[41] or ammonia.[42]

Systems with other sulphates

System: Na_2SO_4-$Al_2(SO_4)_3$.

The anhydrous system was examined by Steele[43] to ascertain if the materials obtained by evaporating Na_2SO_4 + $Al_2(SO_4)_3$ to dryness and heating to 400°C. were mixtures or solid solutions of new compounds. *X*-Ray analysis showed no lines characteristic of $Al_2(SO_4)_3$ or Na_2SO_4 but a new pattern due to $NaAl(SO_4)_2$ or $Na_3Al(SO_4)_3$.

The aqueous system[44] showed the compounds $Na_2SO_4,10H_2O$, $Al_2(SO_4)_3,18H_2O$ and $Na_2SO_4,Al_2(SO_4)_3,24H_2O$ stable at 25°C. The latter salt effloresces readily in air at room temperatures.

System: Na_2SO_4-$BeSO_4$.

The phase diagram for the aqueous system[45] shows Na_2SO_4 (thénardite), $Na_2SO_4,10H_2O$, $3Na_2SO_4,BeSO_4$, $BeSO_4,2H_2O$ and $BeSO_4,4H_2O$.

System: Na_2SO_4-$CaSO_4$.

The ternary system[46] with water is shown in Fig. 7.

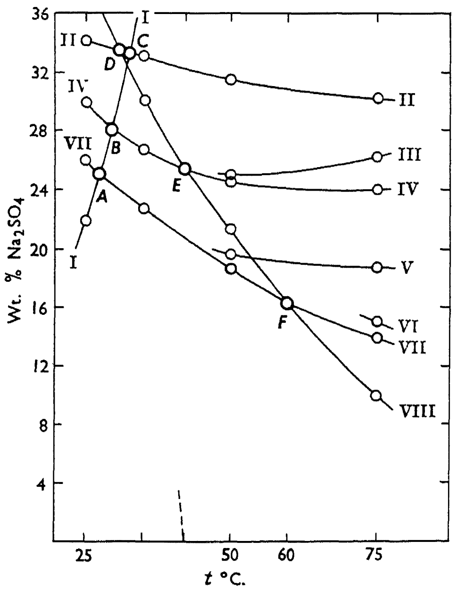


FIG. 7. POLYTHERM OF SYSTEM $CaSO_4$-Na_2SO_4-H_2O

Curve I, gypsum ($CaSO_4,2H_2O$) and mirabilite ($Na_2SO_4,10H_2O$); II, thénardite (Na_2SO_4) and any calcium salt; III, $2Na_2SO_4,CaSO_4,2H_2O$ and $Na_2SO_4,5CaSO_4,3H_2O$; IV, $2Na_2SO_4,CaSO_4,2H_2O$ and gypsum; V, glauberite ($Na_2SO_4,CaSO_4$) and anhydrite ($CaSO_4$); VI, glauberite and $Na_2SO_4,5CaSO_4,3H_2O$; VII, glauberite and gypsum; VIII, $Na_2SO_4,5CaSO_4,3H_2O$ and gypsum

It will be noted that apart from the expected gypsum, anhydrite and glauberite the existence of a labile salt $2Na_2SO_4,CaSO_4,2H_2O$ is confirmed and a new hydrated salt, $Na_2SO_4,5CaSO_4,3H_2O$, is described. The use of the double salt $CaSO_4,Na_2SO_4$ for removal of sodium sulphate by solution and its subsequent decomposition to its component salts on digestion with warm water has been patented.[47]

When a finely ground mixture of anhydrous sodium sulphate and $CaSO_4,5H_2O$ is compressed at 6000 atm., glauberite, the double sulphate, is formed.[48]

System: Na_2SO_4-$CdSO_4$-H_2O.

The compounds $CdSO_4,Na_2SO_4,H_2O$, $CdSO_4,3Na_2SO_4$ and $CdSO_4,Na_2SO_4$ have been shown to exist.[49]

System: Na_2SO_4-$Ce_2(SO_4)_3$-H_2O.

The compounds $Ce_2(SO_4)_3,Na_2SO_4,2H_2O$ and $4Ce_2(SO_4)_3,5Na_2SO_4,8H_2O$ have been shown to exist;[50] the former is stable in contact with solutions containing 0·14–7·0% Na_2SO_4 and 0·35% $Ce_2(SO_4)_3$. Both compounds lose water only when strongly heated e.g. to 400°C.

System: Na_2SO_4-$CoSO_4$-H_2O.

The general characteristics of the system are shown in Fig. 8; the anhydrous salts, and the hydrate $Na_2SO_4,CoSO_4,4H_2O$ are those most commonly met with,[51-53] and the hydrate has been shown to have a constant composition.[54]

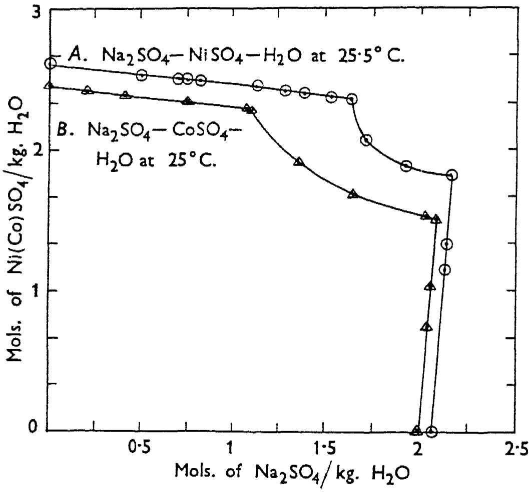


FIG. 8. SYSTEMS Na_2SO_4-Ni(Co)SO_4-H_2O

System: Na_2SO_4-$CuSO_4$-H_2O.

The principal compound[49] is $Na_2SO_4,CuSO_4,3H_2O$ which appears to have a constant composition.[55]

System: Na_2SO_4-$FeSO_4$-H_2O.

The principal compounds[49] are $Na_2SO_4,FeSO_4,H_2O$; $Na_2SO_4,FeSO_4,2H_2O$; $3Na_2SO_4,FeSO_4$.

System: Na_2SO_4-H_2SO_4-H_2O.

Fig. 9 shows the main features of this system.[56] The two compounds $NaHSO_4$ and $Na_3H(SO_4)_2$ appear to be the only compounds, although the monohydrates $NaHSO_4,H_2O$ and $NaH_3(SO_4)_2,H_2O$ have been claimed as entities.[57] Some confirmation of their existence was obtained by Okuno[58] in an extensive survey of the phase diagram from 5°–25°C. Okuno determined the densities

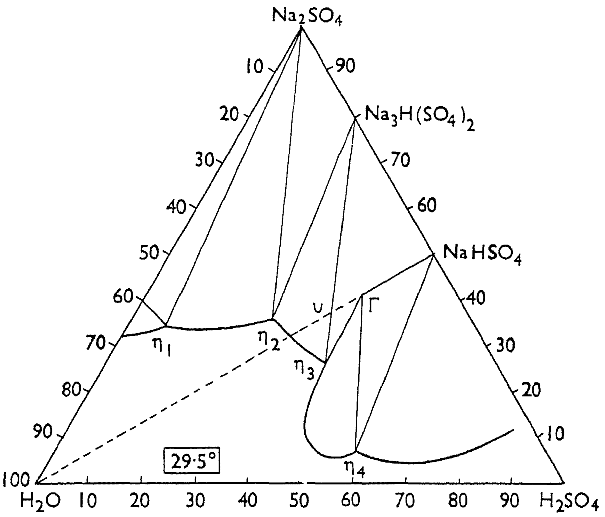


FIG. 9. THE SYSTEM Na_2SO_4-H_2SO_4-H_2O

of the various components and his results are given in Table II.

TABLE II.- DENSITIES OF THE Na_2SO_4-H_2SO_4-H_2O SYSTEM COMPONENTS

Formula	Hydration (mols. H_2O)	D_{20}^{20}
Na_2SO_4	10	1·469
Na_2SO_4	-	2·673
$NaHSO_4$	-	2·476
$NaHSO_4$	1	2·117
$NaH_3(SO_4)_2$	1	2·227
$Na_3H(SO_4)_2$	-	2·423

Thermodynamic data for the reaction $2NaHSO_4(s) \rightarrow Na_2S_2O_7(s) + H_2O(g)$ are:-

$$\log P_{mm.} = -(4303{\cdot}9/T) + 10{\cdot}7436$$
$$F = 19647 - 0{\cdot}48368T \log T + 0{\cdot}00095T + 0{\cdot}00000037T^2 - 34{\cdot}53T^3$$

For the reaction $Na_2S_2O_7(s) \rightarrow Na_2SO_4(s) + SO_3(g)$:-

$$\log P_{mm.} = -(7132{\cdot}44/T) + 12{\cdot}125$$

Luk'yanova[60] has claimed the existence of several additional compounds at higher sulphuric acid concentrations, namely $Na_2SO_4,4{\cdot}5H_2SO_4$ and a metastable $Na_2SO_4,5{\cdot}5H_2SO_4$, thus confirming the work of Kendall and Landon[61] on the former structure.

At one time nitre-cake (a mixture of $NaHSO_4$ with some Na_2SO_4) was a considerable by-product from nitric acid production and it was considered feasible to work it up for sodium sulphate and sulphuric acid.[59]

System: Na_2SO_4-K_2SO_4-H_2O.

This system is simple and shows the definite compound $Na_2SO_4,3K_2SO_4$ (glaserite) which is capable of forming solid solutions in Na_2SO_4 until K:Na = 1:2·44 (25°C.).[62-64] The lattice dimensions for glaserite[65] have been determined at 25°C. as a_0,5·66; c_0,7·33 A.; c/a 1·295. Bredig[66,67] has studied the hexagonal symmetry of glaserite above and below its transition temperature and, finding no change, concludes that $K_3Na(SO_4)_2$ and other alleged double salts of the type A_2XO_4 are in reality only solid solutions.

System: Na_2SO_4-RSO_4-H_2O (R = Lanthanon element).

Zambonini, in a long study of double sulphates, examined the aqueous systems of sodium sulphate and the sulphates of neodymium,[68] praseodymium,[69] lanthanum[70] and cerium (see page 1012). The solid phases characterised are shown in Table III.

TABLE III.- SOLID PHASES FROM AQUEOUS SODIUM SULPHATE - RARE EARTH SULPHATES

Na_2SO_4 (mols.)	R	R_2SO_4 (mols.)	H_2O (mols.)
1	Nd	1	2
5	Nd	4	8
4	Nd	3	6
3	Nd	2	5
4	Pr	5	8
1	Pr	1	2
1	La	1	2

System: Na_2SO_4-$MgSO_4$-H_2O.

Nearly all investigations[71,72] of this system have been directed towards effecting a direct separation of the two sulphates of astrakhanite (Na_2SO_4, $MgSO_4$,$4H_2O$) without the intervention of a third salt. It has been shown[73] that on heating at 105°C. astrakhanite loses two molecules of water, passing into löweite, and that at 215°C. dehydration is complete, giving anhydrous astrakhanite; at 625°C., the latter is converted to a polymorphic form. The rate of formation of stable double salts in the aqueous-Na_2SO_4-H_2SO_4 system is extremely slow, but their formation can be followed by optical means.[74]

Fröhlich has given a critical survey of this system.[75]

System: Na_2SO_4-$MnSO_4$-H_2O.

The main features of this system[76,77] are shown in Fig. 10. No double

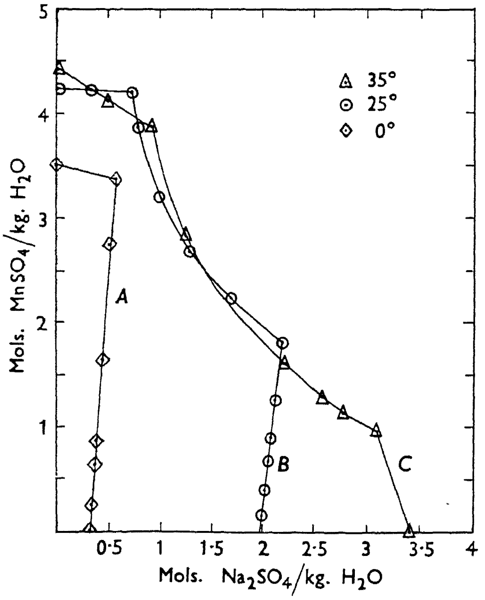


FIG. 10. THE SYSTEM Na_2SO_4-$MnSO_4$-H_2O

salt is formed at 0°C. and the most characteristic double salt at higher temperatures is $Na_2SO_4,MnSO_4,2H_2O$. No indications of the salt $Na_2SO_4,MnSO_4,4H_2O$ claimed by Schreinemakers and Provije[78] were found; this was confirmed by Benrath,[79,80] who, however, states that the double sulphate $3Na_2SO_4,MnSO_4$ is stable above 35°C.

System: Na_2SO_4-$NiSO_4$-H_2O.

The only characteristic double salt of this system is $Na_2SO_4,NiSO_4,4H_2O$.[49,51,52]

System: Na_2SO_4-UO_2SO_4-H_2O.

There appear to be two double salts in this system:[81] $Na_2SO_4,UO_2(SO_4),3H_2O$ and $2Na_2SO_4,UO_2(SO_4)_2 3H_2O$.

System: Na_2SO_4-$ZnSO_4$-H_2O.

This system was investigated by Benrath[79,80] who observed the phases $Na_2SO_4,ZnSO_4,6H_2O$ and $3Na_2SO_4,ZnSO_4$. Caven and Johnson[76] obtained the isotherms of Fig. 11, confirming this view.

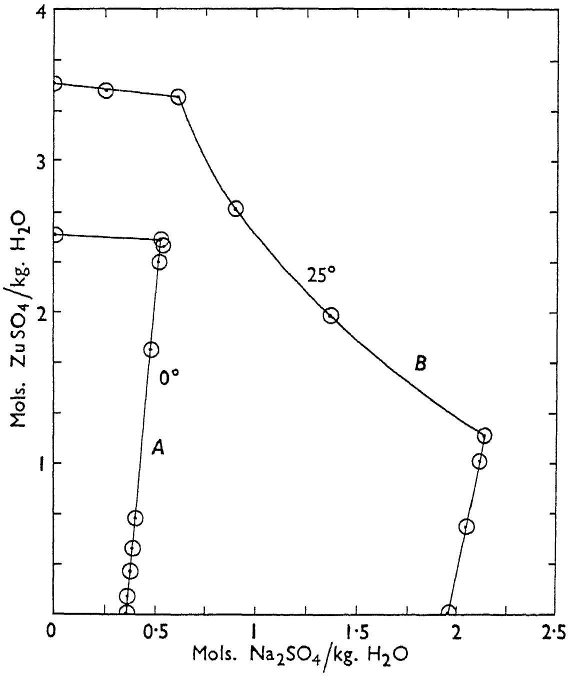


FIG. 11. THE SYSTEM Na_2SO_4-$ZnSO_4$-H_2O

Work on systems comprising sodium sulphate, water and a single salt (not a sulphate) is summarised in Table IV.

TABLE IV.- SOME TERNARY SYSTEMS INVOLVING Na_2SO_4

Substances in addition to Na_2SO_4-H_2O	Temp. Range Studied in °C.	Phases and Compounds characterised	Refs.	Notes
Aluminium selenate ($Al_2(SeO_4)_3$)	25	-	82, 83	

continued on following page

TABLE IV.- continued

Substances in addition to Na_2SO_4-H_2O	Temp. Range Studied in °C.	Phases and Compounds characterised	Refs.	Notes
Ammonia (NH_3)	0–50	-	84	The isotherms have two branches Na_2SO_4, $10H_2O$ and Na_2SO_4. The dehydration temp. of the decahydrate increases with concn. of NH_3
Ammonium bicarbonate (NH_4HCO_3)	-17 -10 -5·9 -5 0 7 15	$Na_2SO_4,(NH_4)_2SO_4,4H_2O$ (I) $I+Na_2SO_4,10H_2O+(NH_4)_2SO_4$ $I+Na_2SO_4,10H_2+NaHCO_3$ $Na_2SO_4,10H_2O+NH_4HCO_3$ + ice	85–89	Theoretically, by combining evaporation with freezing out, it is possible to separate Na_2CO_3 and $(NH_4)SO_4$ completely
Ammonium borate $(NH_4)_2B_4O_7$	0–50	Reciprocal pair only	90	
Ammonium carbonate $(NH_4)_2CO_3$	32·5	Reciprocal pair only	91, 92	
Ammonium nitrate NH_4NO_3	100–150	-	92a	A ternary point exists at 118° where Na_2SO_4, $NaNO_3$ and mixed crystals are in equilibrium
Ammonium perchlorate NH_4ClO_4	25, 60	-	93	
Calcium phosphate $CaHPO_4,2H_2O$ (Brushite)	23·5	$CaHPO_4$ (monetite)	94	
Calcium tetraborate CaB_4O_7	-	$Na_2B_4O_7,2CaSO_4$ $Na_2B_4O_7,2CaB_4O_7$ $2Na_2SO_4,CaSO_4$	95 95	
Magnesium chloride $MgCl_2$	0–83	$Na_2SO_4,MgSO_4,4H_2O$ (Astrakhanite)	96, 97	The temperature of simultaneous saturation of water by NaCl, Na_2SO_4 and $Na_2SO_4,10H_2O$ is lowered from 17·9 to 16·2°C. by $MgCl_2$
Magnesium molybdate $MgMoO_4$	25	-	98	
Magnesium nitrate $MgNO_3$	15,25 50,97	None	98a	

continued on following page

TABLE IV.- continued

Substances in addition to Na_2SO_4-H_2O	Temp. Range Studied in °C.	Phases and Compounds characterised	Refs.	Notes
Oxalates Na oxalate $C_2O_4Na_2$	25,60	-	99	
Oxalic acid $C_2H_2O_4$	-	$Na_3H_3(SO_4)_2.C_2O_4$	100	Acid sodium sulphate-oxalate
Potassium permanganate $KMnO_4$	25	-	101	Mainly on account of the solubility of $KMnO_4$ in aqueous Na_2SO_4
Sodium bicarbonate $NaHCO_3$	0 20 25 30 45	-	102	Each isotherm consists of two parts. Below 30° $Na_2SO_4.10H_2O$ separates; at 45° Na_2SO_4 is the solid phase
Sodium bromate $NaBrO_3$	45 25	Three series of mixed crystals	103 104	Above 30° a single solid solution containing up to 18·5% $NaBrO_3$ at 52° is formed
Sodium carbonate Na_2CO_3 (See Fig. 12)	0–45 50	$2Na_2SO_4,Na_2CO_3$ (Berkeite)[107]	105 106 109 110	Berkeite forms orthorhombic crystals of the rhombic-bipyramidal class; *a*:*b*:*c* = 0·579:1: 1·213[108]
Sodium chlorate $NaClO_3$	15 25 45 75	$3Na_2SO_4,NaClO_3$	111	
Sodium chloride NaCl (See Fig. 13)	25	No compounds	112-117	A strong solution of brine salts out anhydrous sodium sulphate from the decahydrate (see p. 999).
Sodium chromate Na_2CrO_4 (The anhydrous Na_2SO_4-$NaCrO_4$ diagram is shown in Fig. 14)	28 31 33	Solid solutions only	120-121	One group of workers claim to have established[118] the existence of $Na_2SO_4,6H_2O$ in mixed crystals with $Na_2CrO_4,6H_2O$. Others[119] claim $Na_2SO_4,4H_2O$ under analogous circumstances

continued on following page

TABLE IV.- continued

Substances in addition to Na_2SO_4–H_2O	Temp. Range Studied in °C.	Phases and Compounds characterised	Refs.	Notes
Sodium dichromate $Na_2Cr_2O_7$	0,15 25,40 60,80 98	None	122	Pure $Na_2Cr_2O_7$ cannot be obtained by recrystallization if sulphates are present
Sodium fluoride NaF	0–80	Na_2SO_4,NaF	123	A method of separating Na_2SO_4 from Na_2CO_3
Sodium ferrocyanide $Na_4Fe(CN)_6$	0–50	-	124	
Sodium hydroxide NaOH	0,10 18,25 30	(Probable)Na_2SO_4,NaOH	125-131	The double compound is classed as an 'orthosulphate'; it meets incongruently at 480° C.
Sodium iodate $NaIO_3$	25 29·5 35,50	$3Na_2SO_4$,$NaIO_3$ $4Na_2SO_4$,$NaIO_3$	132	
Sodium iodide NaI	18-20	-	133	
Sodium molybdate Na_2MoO_4	0,8·5, 12·1 20,28	None	134-136	Quadrupole points at 248 and 9·8° C.
Sodium nitrate (See also Fig. 15)	25–90	Na_2SO_4,$NaNO_3$,H_2O (The existence of a double salt $4Na_2SO_4$, $3NaNO_3$ has not been confirmed[137]	138-141	Triple point for darapskite 24·2-24·5° C.
Sodium phosphate	150-350	Na_2SO_4,$2Na_3PO_4$ Na_2SO_4,$5Na_3PO_4$	142	A new 'bomb' method for determining isotherms at high temperatures is described
Sodium phthalate $Na_2C_8H_4O_4$	0–25	-	143	Quintuple point is 23° C. The principal hydrate is $2Na_2C_8H_4O_4$,$7H_2O$
Sodium silicofluoride Na_2SiF_6	17–208	-	144	A study of the solubility of Na_2SiF_6 in aqueous sodium sulphate

continued on following page

TABLE IV.- continued

Substances in addition to Na_2SO_4-H_2O	Temp. Range Studied in °C.	Phases and Compounds characterized	Refs.	Notes
Sodium soaps	15-25	- (liquid/liquid system)	145, 146	A study of the salting out effect of Na_2SO_4 solutions on the sodium salts of stearic, oleic and palmitic acids
Sodium sulphite Na_2SO_3	40,60 and 0-37·5	no compounds detected	147, 148	Two series of mixed crystals are formed, one corresponding to the decahydrate and the other to the heptahydrates
Sodium thiosulphate $Na_2S_2O_3$	0·8,18 25,40	-	149	Mixed crystals of the pentahydrates were shown to exist at all four temperatures
Sulphur dioxide	10-90	-	150	A study of the solubility of SO_2 in sodium sulphate solutions

In Table V is summarised the work done on systems containing two compounds in addition to sodium sulphate and water.

TABLE V.- SYSTEMS CONTAINING TWO COMPOUNDS IN ADDITION TO SODIUM SULPHATE AND WATER

Substances in addition to Na_2SO_4-H_2O	Temp. Range Studied (°C.)	Phases and compounds characterized	Refs.	Notes
Ammonia Ammonium sulphate	0-15	$Na_2SO_4,(NH_4)_2SO_4,4H_2O$	151- 152	Saturation of solutions of sodium sulphate with ammonia lowers the solubility of sodium sulphate
Ammonia Sodium chloride	0-50	-	153	ditto
Ammonium bicarbonate Sodium bicarbonate	-	$Na_2SO_4,(NH_4)_2SO_4,4H_2O$	154	A study of the best conditions for industrial conversion of sodium sulphate to carbonate

continued on following page

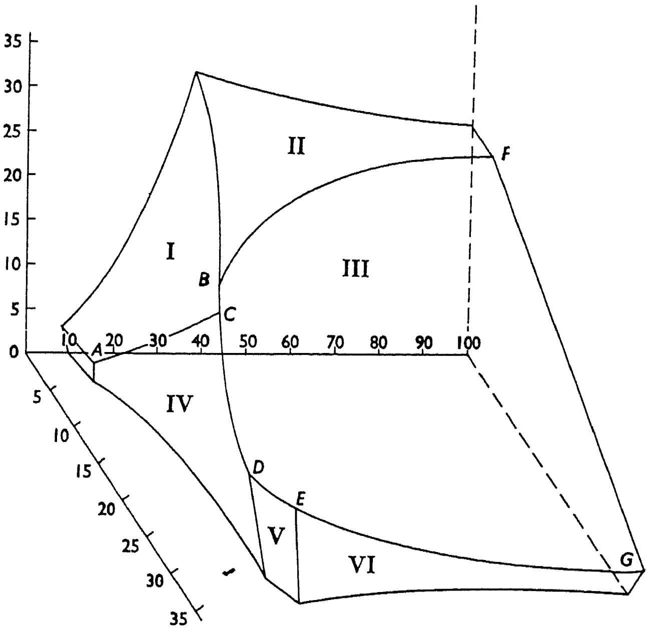
TABLE V.- continued

Substances in addition to Na_2SO_4-H_2O	Temp. Range Studied in °C.	Phases and Compounds characterized	Refs.	Notes
Ammonium sulphate Potassium sulphate	0,25 40	$Na_2SO_4.(NH_4)_2SO_4.H_2O$	155	
Calcium carbonate Calcium sulphate	200-300	-	156	Gives the lowering of the CO_3/SO_4 ratio due to Na_2SO_4
Calcium sulphate Potassium sulphate	-	-	157	
Calcium sulphate Magnesium sulphate (anhydrous system)	200-800	A single ternary eutectic at 650° exists, for 53% Na_2SO_4 40% $MgSO_4$, 7% $CaSO_4$	158	$CaSO_4+MgSO_4$ form a simple eutectic system
Calcium sulphate Sulphuric acid	45,60 80	$Na_2SO_4.CaSO_4$	159	
Copper sulphate Potassium sulphate (anhydrous system)	up to 850	$Na_2SO_4.3K_2SO_4$	160	The blue variety of the mineral aphthitalite is a solid solution of $CuSO_4$ in $Na_2SO_4.3K_2SO_4$
Ethanol H_2O(and with free H_2SO_4)	30 36	- (See Fig. 16)	161 161a	Ethanol of more than 56·8% strength dehydrates sodium sulphate decahydrate at 30°C. H_2SO_4 leads to presence of $EtHSO_4$
Magnesium chloride	0,10	-	162	
Sodium nitrate	25,50 75,100		163	
Potassium chloride Sodium nitrate (anhydrous system)	200-500	-	164	Between 249 and 504° the heat capacity/t° curve is linear and is higher than the value calculated additively for the solid components
(aqueous system)	25,50	Many solid solutions	165 166	The diagram is exceedingly complex and many points have not been determined experimentally
Lead sulphate Potassium sulphate (anhydrous system)	400-900	$K_2SO_4.PbSO_4$ $Na_2SO_4.PbSO_4$ $K_2SO_4.2PbSO_4$ $Na_2SO_4.2PbSO_4$	167	

continued on following page

TABLE V.- continued

Substances in addition to Na_2SO_4-H_2O	Temp. Range Studied in °C.	Phases and Compounds characterized	Refs.	Notes
(aqueous system)	15,18 20,25 30	-	168 169	A study of the solubility of lead sulphate in electrolytes
Sodium carbonate	25	Na_2CO_3,$NaHCO_3$,$2H_2O$	170,188	
Sodium bicarbonate			171	
Sodium chromate		-	172	Three clear fields of crystallization show crystn. of $NaNO_3$ and the α and β forms of the solid solns. of Na_2SO_4-Na_2CrO_4
Sodium nitrate	200-900		173	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F
G
I
II
III
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VI

FIG. 12. THE SYSTEM Na_2SO_4-Na_2CO_3-H_2O

Systems with more than two components in addition to sodium sulphate and water are summarised in Table VI.

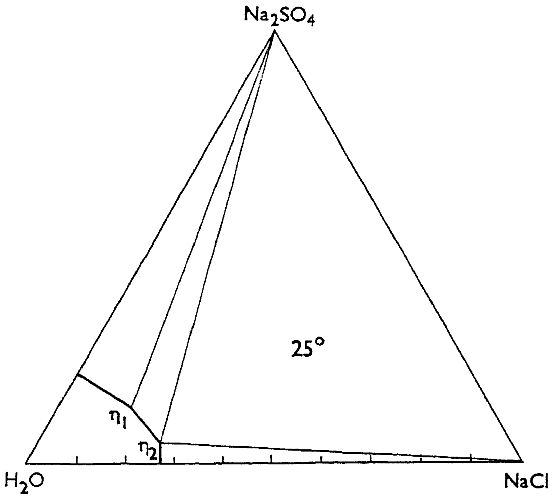

FIG. 13. THE SYSTEM Na_2SO_4-NaCl-H_2O

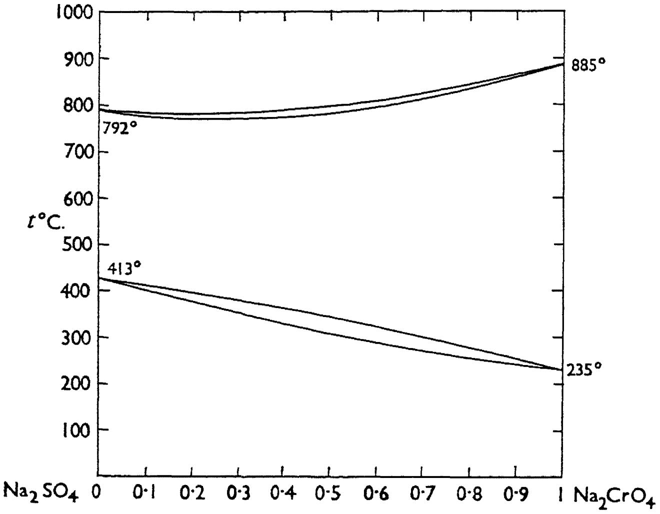

FIG. 14. THE SYSTEM Na_2SO_4-Na_2CrO_4

TABLE VI.- SYSTEMS WITH MORE THAN TWO COMPONENTS IN ADDITION TO Na_2SO_4 AND H_2O

Substances in addition to Na_2SO_4-H_2O	Temp. Range Studied in °C.	Phases and Compounds characterized	Refs.	Notes
Calcium carbonate Calcium sulphate Sodium carbonate	7–38	-	174	A solubility study

continued on following page

TABLE VI.- continued

<table>
<tr><th>Substances in addition to $Na_2SO_4-H_2O$</th><th>Temp. Range Studied in °C.</th><th>Phases and Compounds characterized</th><th>Refs.</th><th>Notes</th></tr>
<tr><td>Hydrochloric acid
Sodium hydrogen sulphate
Sodium chloride</td><td>-</td><td>-</td><td>175</td><td>The following data were obtained $\log p_{mm.} = -2241{\cdot}2/T - 8{\cdot}251$</td></tr>
<tr><td></td><td></td><td></td><td>176</td><td>Thermodynamic relations for the equilibria were determined</td></tr>
<tr><td>Hydrochloric acid
Sodium chloride
Sulphuric acid</td><td>-</td><td>-</td><td>177-179</td><td>A method of working up waste Na_2SO_4/H_2SO_4 from the artificial silk industry</td></tr>
<tr><td rowspan="18">Magnesium sulphate
Potassium chloride
Potassium sulphate
(K, Na, Mg, Cl, SO_4, H_2O)</td><td colspan="4">Fig. 17 shows the general picture[180] of this most complex system and Fig. 18 the details of the magnesium chloride section. It is an excellent example of complex phase relations. The following phases were isolated:-</td></tr>
<tr><td></td><td></td><td colspan="2">Ref. letter in Figs. 17 & 18</td></tr>
<tr><td>Na_2SO_4</td><td>thénardite</td><td colspan="2">A</td></tr>
<tr><td>$Na_2SO_4,10H_2O$</td><td>mirabilite</td><td colspan="2">A</td></tr>
<tr><td>$MgSO_4,H_2O$</td><td>kieserite</td><td colspan="2">B</td></tr>
<tr><td>$MgSO_4,6H_2O$</td><td>-</td><td colspan="2">B</td></tr>
<tr><td>$MgSO_4,7H_2O$</td><td>reichardite</td><td colspan="2">B</td></tr>
<tr><td>K_2SO_4</td><td>-</td><td colspan="2">C</td></tr>
<tr><td>NaCl</td><td>halite</td><td colspan="2">P</td></tr>
<tr><td>$MgCl_2,6H_2O$</td><td>bischofite</td><td colspan="2">Q</td></tr>
<tr><td>KCl</td><td>sylvite</td><td colspan="2">R</td></tr>
<tr><td>$Na_2SO_4,MgSO_4,4H_2O$</td><td>astrakhanite</td><td colspan="2">D_1</td></tr>
<tr><td>$Na_2SO_4,2H_2SO_4$</td><td>glaserite</td><td colspan="2">D_2</td></tr>
<tr><td>$K_2SO_4,MgSO_4,2H_2O$</td><td>leonite</td><td colspan="2">D_3</td></tr>
<tr><td>$K_2SO_4,MgSO_4,6H_2O$</td><td>picromerite</td><td colspan="2">D_3</td></tr>
<tr><td>$KCl,MgCl_2,6H_2O$</td><td>carnallite</td><td colspan="2">D_4</td></tr>
<tr><td>$KCl,MgSO_4,3H_2O$</td><td>kainite</td><td colspan="2">T_1</td></tr>
<tr><td colspan="4"></td></tr>
<tr><td>Phosphoric acid
Sulphuric acid
Sodium phosphate</td><td>-</td><td>-</td><td>181</td><td>A series of pH measurements at various concentrations</td></tr>
<tr><td>Potassium chloride
Potassium sulphate
Sodium chloride</td><td>0-50</td><td>$Na_2SO_4,3K_2SO_4$
(no triple salts)</td><td>182-184</td><td></td></tr>
<tr><td>Sodium carbonate
Sodium chloride
Sodium hydroxide</td><td>50</td><td>$2Na_2SO_4,Na_2CO_3$</td><td>185-188</td><td></td></tr>
</table>

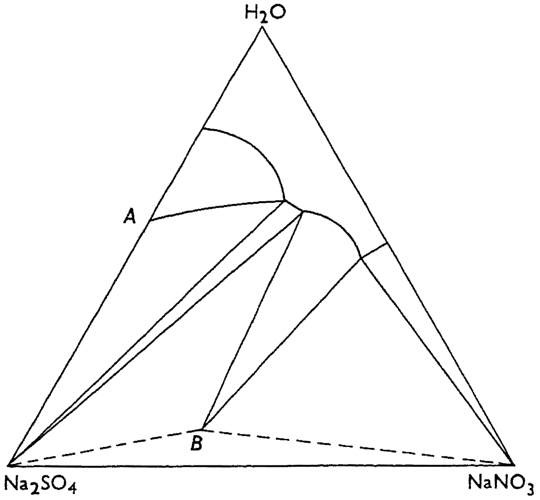

FIG. 15. THE SYSTEM Na_2SO_4-$NaNO_3$-H_2O
A = Na_2SO_4,$10H_2O$
B = Na_2SO_4,$NaNO_3$,H_2O

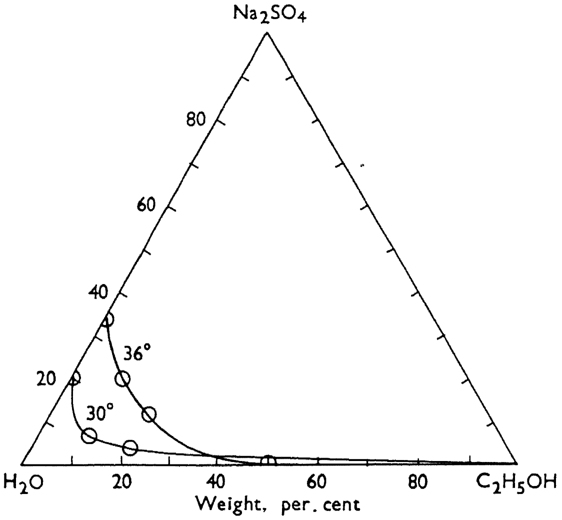

FIG. 16. THE SYSTEM ETHANOL-Na_2SO_4-H_2O AT TEMPERATURES ABOVE AND BELOW THE TRANSITION POINT

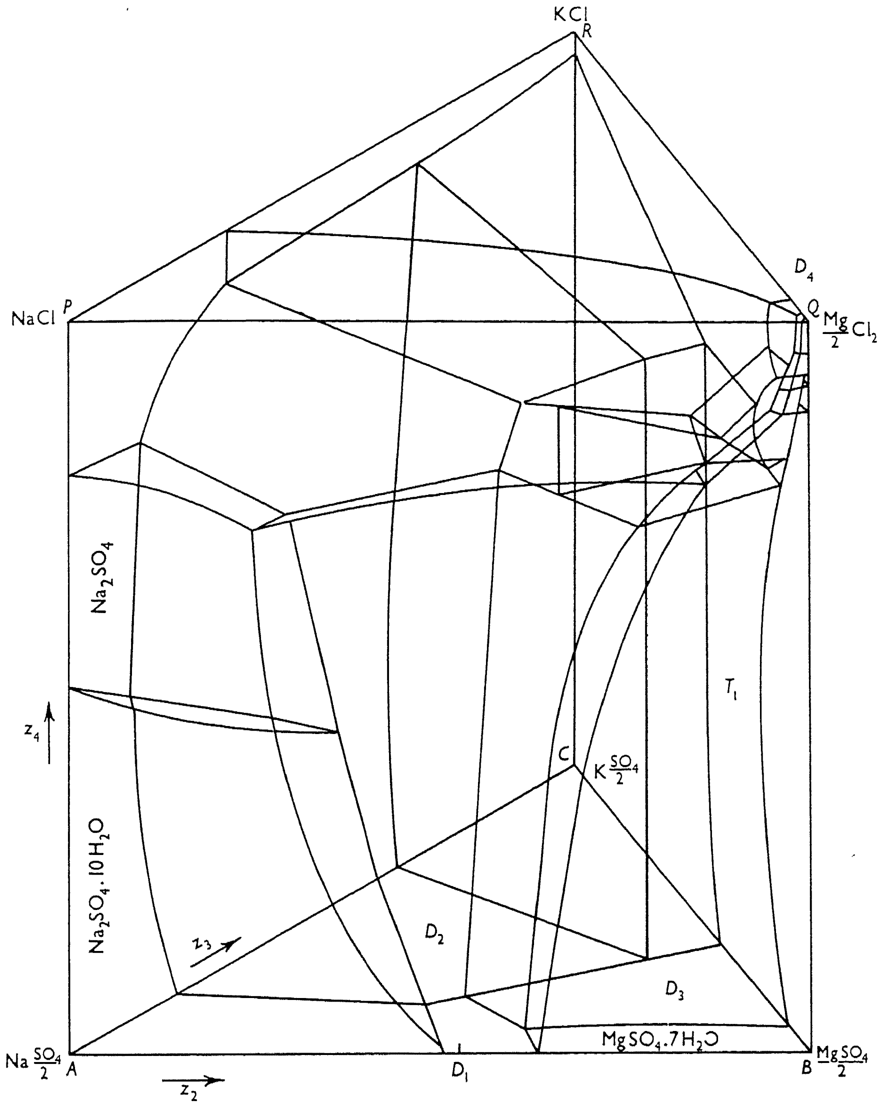
KCl
R
NaCl
P
D_4
Q
$\frac{Mg}{2}Cl_2$
Na_2SO_4
$Na_2SO_4.10H_2O$
z_4
T_1
C
$K\frac{SO_4}{2}$
z_3
D_2
D_3
$MgSO_4.7H_2O$
$Na\frac{SO_4}{2}$
A
D_1
B
$\frac{MgSO_4}{2}$
z_2

FIG. 17. QUINARY SYSTEM FORMED BY QUATERNARY SYSTEM OF THE THIRD KIND PLUS WATER. AMOUNT OF WATER ELIMINATED SOMEWHAT SIMPLIFIED IN THE NEIGHBOURHOOD OF Q

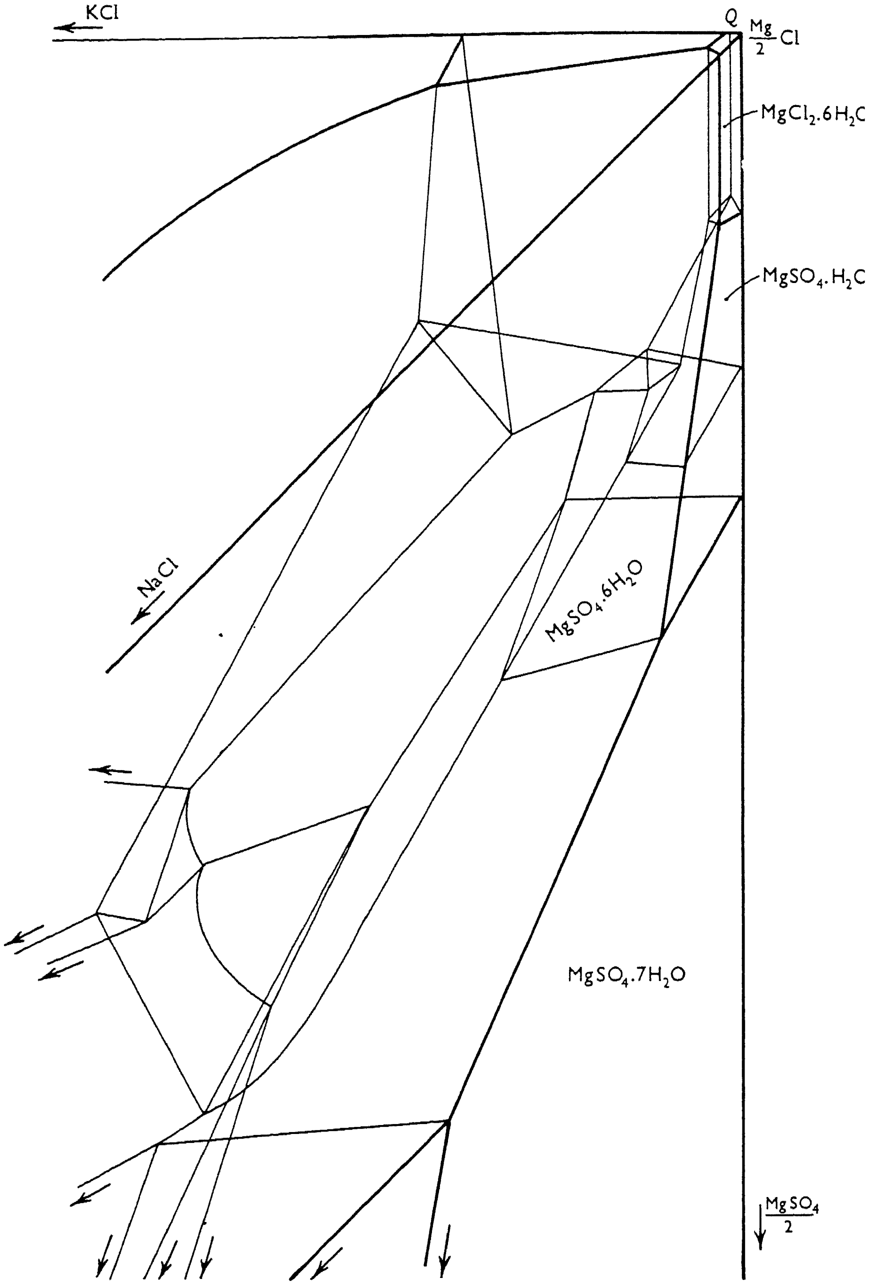
KCl
Q
$\frac{Mg}{2}$Cl
MgCl$_2$.6H$_2$C
MgSO$_4$.H$_2$C
NaCl
MgSO$_4$.6H$_2$O
MgSO$_4$.7H$_2$O
$\frac{MgSO_4}{2}$

FIG. 18. DETAIL OF THE MgCl$_2$-CORNER (THE PRISM HAS BEEN ROTATED, SO THAT NOW QR IS IN THE PLANE OF THE PAPER). POINTS 14, 16, 17, AND 18 HAVE NOT BEEN EXPERIMENTALLY DETERMINED

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PHYSICAL PROPERTIES

The work of Tutton[1] and of Ogg and Hopwood[2] on the *X*-ray analysis of the crystal structure of sodium sulphate was discussed in the original Treatise (Mellor,II,660). Ogg[3] later calculated the space group $V_h 16$ for alkali metal sulphates and showed that the data agreed with those of Tutton (ibid.) and of Taylor and Boyer.[4] The crystal structure of anhydrous sodium sulphate has been studied by Colby[5] and by Zachariasen and Ziegler.[6] They agree that the X-ray data imply an orthorhombic cell of space group $Fddd(V_h^{24})$. Their values, respectively, for the unit cell are a = 5·182, 5·85; b = 12·30, 12·29; c = 9·82, 9·75 (all in A.). Each sulphur atom is surrounded by an almost complete tetrahedron of oxygen atoms (S–O=1·49 A.; O–O=2·43 A.). Colby postulates an 8-molecule unit, and Zachariasen and Ziegler a 4-molecule unit. The results of Gossner and Mussgnug[7] do not agree closely with either of these views and careful repetition of the work by Frevel[8] using sodium sulphate–III gave values for an orthorhombic unit cell of $4Na_2SO_4$ as a = 5·59 ± 0·02; b = 8·93 ± 0·02; c = 6·98 ± 0·02 A. The results of Das Gupta[9,10] are again different, and lead to the conclusion that anhydrous sodium sulphate–III belongs to the tetragonal system, with sixteen molecules to the unit cell. Shoji[11] has called attention to the allotropic transformations of anhydrous sodium sulphate which may account for the discrepancies in X-ray data. An examination of the fibrous form of anhydrous sodium sulphate was made by Matsumoto.[12]

Bentivoglio[13] investigated the rate of growth of a series of salts including sodium sulphate and showed that unlike faces grew at different (linear) rates but that similar faces had the same linear rate of growth. Hence, a misshapen crystal, grown under uniform conditions, tends toward, but does not reach, the ideal form. The rate of crystallization of sodium sulphate decahydrate from supersaturated solutions has been measured[14] by filling long capillary tubes, maintained at constant temperature, with the supersaturated solution and inoculating one end. The velocity v alters with temperature, passing through a minimum and maximum, and is proportional to C^2 (where the supersaturated solution contains C% of Na_2SO_4). v is independent of the diameter of the tube (between 3 and 11 mm.) and is raised by the presence of 0·1% of gelatin. Devaux[15] has observed that when films of sodium sulphate solution crystallize on pure mercury two zones are formed.

Sodium sulphate exhibits tribo-, thermo- and crystallo-luminescence. Triboluminescence is greatly increased in intensity by exposure to radium.[16] Kuznetsov[17] has shown that neither sodium sulphate nor potassium sulphate shows crystalloluminescence alone and in the absence of impurities but when crystallized together invariably show this phenomenon whether the solutions are old or new or are prepared from redissolved crystals. The intensity of the light emitted increases with the temperature at which separation occurs.

The thermoluminescence of sodium sulphate containing traces of manganese has been studied[18] and various metal sulphates with sodium sulphate ($PbSO_4$, Na_2SO_4; $BaSO_4$, Na_2SO_4; $SrSO_4$, Na_2SO_4) have been shown to be luminophors in the presence of 0·1% of samarium as activator;[19] these observations probably relate to the 'corpuscular phosphorescence' of sodium sulphate observed by Schmidt.[20] In the course of experiments on light scattering by sodium sulphate solutions their fluorescence was observed.[21]

Andreae's pycnometer method[23] applied to $Na_2SO_4,10H_2O$ gave a value[22] 1·4665 for the density at 20·0 °C., identical with that obtained by the suspension method; these figures are comparable with the values, 1·469 at 3·9° C. and 1·455 at 26·5° C., obtained by earlier workers (Mellor, II, 662). The compressibility[24] of anhydrous sodium sulphate (k; relative volume change or bulk compression) is given by

$$k = (237{\cdot}1p - 2{\cdot}38p^2)10^{-5}$$

where p is the pressure in kilobars. The dielectric constant of anhydrous sodium sulphate is 7·90 and of the decahydrate 5·00. The molar polarization for each water molecule in the decahydrate has been compared[25] with that of the corresponding molecules in the hydrated forms of copper sulphate and magnesium sulphate and is invariant and within ±5% of the values calculated by the Clausius–Mosotti equation. Kamiyoshi[26] has confirmed the value

5·00 for the decahydrate using a powder-cell method.

Revised values[27] have been given for the refractivity of sodium sulphate by Walff and Schaller; they ascribe the existence of ΔR (difference between observed and calculated mol. refractivity) to the electrostatic effect of neighbouring ions. The molecular refraction of sodium sulphate is 14·927 at 22°C.[28]

The specific heat of sodium sulphate in powder form,[29] is given by $C_p = A + (B \times 10^{-3}\theta)$ where A and B are 28·24 and 52·07 and θ is the temperature. The value obtained experimentally for the heat of transition of anhydrous sodium sulphate varies with the history of the sample. The following values were obtained:-

Heating	Ht. of transition (g.-cal./mole) at 194·5–290·5°C.
1	–2587 ± 4·55
2	–2020·5 ± 50·5
3	–2076 ± 25·5

Meissner has shown that the m.p. of substances, including sodium sulphate, is lowered by subdivision, largely owing to differences in surface energies.[30] Using lamellae he showed that the difference between the surface energies of crystal and liquid forms (A_0–A_0') is given by:-

$$A_0 - A_0' = \frac{T_1 - T_2}{T_0} . \frac{RQ}{2} . \frac{d_1 d_2}{(d_1 - d_2)}$$

where T_0 is the normal m.p., T_1 and T_2 are the m.p. of lamellae of thickness d_1 and d_2, R is the heat of fusion and Q the density of the liquid form. Differences in lamellar thickness of from 10μ to 0·8μ depressed the m.p. of sodium sulphate by 0·258°C., pointing to a difference in surface energy of 59 ergs.

The heat contents (in g.-cal./mole) for some of the forms of sodium sulphate are given in Table VII.

TABLE VII.- HEAT CONTENT OF VARIOUS FORMS OF SODIUM SULPHATE

Form	Equation	Temp. °K.
Na_2SO_4 (I)	$H_T - H_{298{\cdot}16} = 29{\cdot}06T + 9{\cdot}67 \times 10^{-3}T^2 - 7837$	514–1157
Na_2SO_4 (III)	$H_T - H_{298{\cdot}16} = 15{\cdot}54T + 26{\cdot}40 \times 10^{3}T^2 - 6980$	298–514
Na_2SO_4 (V)	$H_T - H_{298{\cdot}16} = 23{\cdot}50T + 15{\cdot}87 \times 10^{3}T^2 - 8418$	298–450

The heats of transformation of the various forms of sodium sulphate were determined by Coughlin[31] and some results are shown in Table VIII.

TABLE VIII.- HEATS OF TRANSFORMATION OF SOME FORMS OF Na_2SO_4

Form	Heat of transformation (g.-cal./mole)		Temp. °K.
	calc.	obs.	
V III	740 ± 120	735 ± 15	45
III I		1680	514
I (fusion)		5670	1157

The same author gives the heat of solution of Na_2SO_4 (V) in water at 30°C. as –627 ± 3 g.-cal./mole at 0·054 molal. The entropy increment (ΔC_p) for the average heat of solution of 1 mole of Na_2SO_4 in 1050 moles of water is –65·1 ± 6·5 g.-cal./deg. mole.

The effect of sodium sulphate on the consolute temperatures of thallium bromide and potassium nitrate (in the proportion 3:1) is –21°C.[32]

Sodium sulphate as a solvent and a solute

Petit[33] showed that sodium sulphate is a good solvent for studying salt formation between alkali and alkaline-earth sulphates and halides. The cryoscopic constant was found to be 72 and the heat of fusion 5240 g.-cal./mole; the latter figure was estimated at 6100 g.-cal./mole by Flood *et al.*[34] The solubility of barium oxide was studied by the method of isothermal saturation. The solubilities of barium oxide[35] in lithium chloride, lithium sulphate, sodium chloride, sodium sulphate, and potassium chloride diminish in that order, thus supporting Semenchenko's theory of real solutions.

The surface tension (σ) for pure sodium sulphate, alone and in admixture with alkali halides, is given[36] in Table IX.

TABLE IX.- SURFACE TENSION OF SODIUM SULPHATE AND ALKALI HALIDES

Mol.-% Na_2SO_4	Second Salt	ergs σ/cm.^{2}	Temp. °C.
100	-	193·7	900
50	KCl	129·3	900
50	KBr	115·6	900
50	KI	100·8	900

The presence of small amounts of potassium chloride, bromide or iodide leads to great diminution of crystal size when sodium sulphate crystallizes.

The surface tension[37] of aqueous solutions of sodium sulphate was shown by Stocker by the jet method to follow the law:-

$$T = \frac{4(\sigma-\sigma_1)A^2}{\lambda^2} \cdot \frac{[1 + {}^{37}/_{24}(b/a)]}{6 + 10(\pi a/\lambda)^2 + 2{\cdot}5(\pi a/\lambda)^4}$$

where T = surface tension of the solution, σ = density of the liquid, σ_1 = density of the surrounding air, a = radius of the jet, $A = C/\pi a^2$ where C is the velocity of the liquid flow, and b/a = the amplitude. The effect of sodium sulphate on the viscosity of sucrose solutions at 55% sugar strength has been examined;[35] the viscosity increases with increasing salt concentration and with different salts follows the order $PO_4^{3-} > CO_3^{2-} > SO_4^{2-} > Br^-$. The viscosity of sodium sulphate solutions increases more rapidly than the concentration, while with potassium sulphate the opposite effect is observed.[39] In connexion with experiments to examine changes in physical properties at the transition point, the viscosity of sodium sulphate has been carefully examined between 25° and 40°C. The relation between viscosity and concentration at a given temperature is given by[40]

$$\eta = 1 + A\sqrt{C} + BC$$

where at 25°C., $A = 0{\cdot}0155$ and $B = 0{\cdot}357$. Other workers[41,42] have used the relation

$$\eta = A^{c(1 + ac^2)}$$

where A and a are constants. Sodium sulphate has little or no influence on the viscosity of aqueous solutions of potassium dichromate which alone, between 10° and 25°C., has the same viscosity as water.[43] An elaborate study was made of the solubility of sodium sulphate in water-ethylene glycol mixtures, with the purpose of achieving normal behaviour of anhydrous sodium sulphate in evaporator-crystallisers. Owing to the inverted solubility relationships of anhydrous sodium sulphate in water, the crystallization of the material in evaporators is difficult; the separating material tends to form a hard layer on the heating surfaces which lowers heat transfer and makes removal of solids by the normal means virtually impossible. The solubility/density curve is

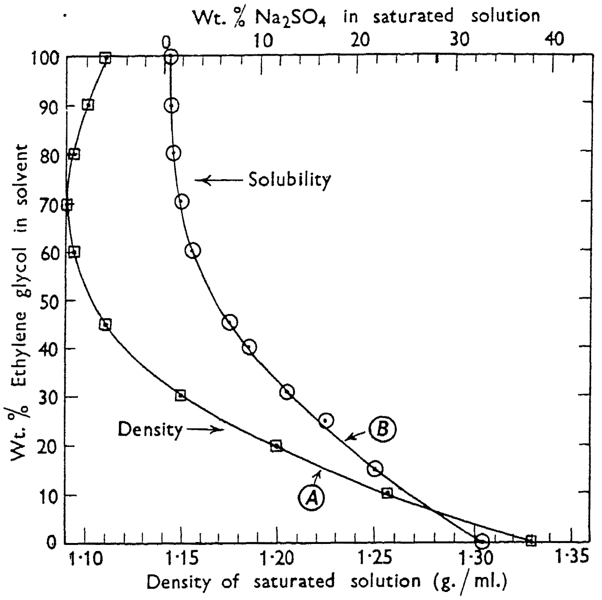

FIG. 19 ETHYLENE GLYCOL-WATER COMPOSITIONS IN THE PRESENCE OF SODIUM SULPHATE

shown in Fig. 19 and the variation of the Na_2SO_4-$Na_2SO_4,10H_2O$ transition temperature with ethylene glycol content is shown in Fig. 20. In Table X are

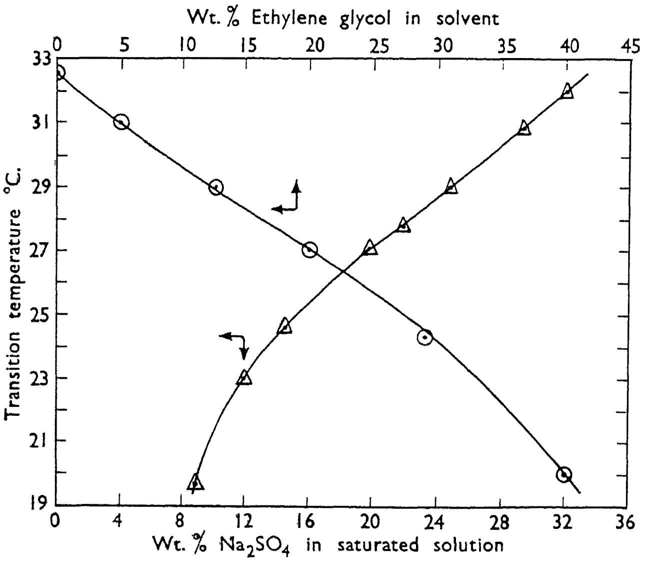

FIG. 20 VARIATION OF Na_2SO_4-$Na_2SO_4,10H_2O$ TRANSITION TEMPERATURE WITH ETHYLENE GLYCOL-WATER COMPOSITION

shown the solubilities of sodium sulphate in aqueous ethylene glycol at temperatures around and above 100°C.

TABLE X.- SOLUBILITIES OF SODIUM SULPHATE IN ETHYLENE GLYCOL WATER MIXTURES

Temp. °C.	Wt.-% glycol	Wt.-% Na_2SO_4 in sat. soln.	Temp. °C.	Wt.-% glycol	Wt.-% Na_2SO_4 in sat. soln.
103·0*	-		108·9*	48·6	
102·6	-	29·622	108·8	48·6	5·528
101·5	-	29·631	106·3	48·6	5·530
100·46	-	29·638	103·15	48·6	5·545
98·85	-	29·663	98·75	48·6	5·554
96·10	-	29·724	111·3*	60·1	
104·5*	10·5		110·95	60·1	3·188
104·3	10·5	22·913	110·13	60·1	3·187
103·5	10·5	22·915	108·95	60·1	3·183
102·8	10·5	22·922	108·10	60·1	3·184
99·75	10·5	22·952	100·00	60·1	3·201
104·9*	18·1		114·40*	67·5	
104·5	18·1	18·477	113·85	67·5	1·975
102·93	18·1	18·462	112·5	67·5	1·986
100·40	18·1	18·477	109·8	67·5	1·997
96·4	18·1	18·516	106·5	67·5	2·003
105·1*	24·2		98·75	67·5	2·034
104·8	24·2	15·189	119·7*	75·5	
103·9	24·2	15·192	119·15	75·5	1·104
103·05	24·2	15·201	118·25	75·5	1·108
99·65	24·2	15·228	115·80	75·5	1·120
106·0*	36·2		112·70	75·5	1·132
105·75	36·2	9·839	108·40	75·5	1·138
104·40	36·2	9·836	103·40	75·5	1·168
103·00	36·2	9·840	100·00	75·5	1·190
101·75	36·2	9·859	124·3*	80·0	
107·1*	41·0		123·45	80·0	0·795
106·65	41·0	7·915	121·50	80·0	0·792
104·50	41·0	7·913	117·25	80·0	0·791
105·60	41·0	7·910	107·20	80·0	0·840
103·50	41·0	7·911	99·30	80·0	0·860
100·00	41·0	7·914	136·3*	90·0	
108·3*	45·5		135·05	90·0	0·421
108·00	45·5	6·624	131·20	90·0	0·413
106·60	45·5	6·611	128·30	90·0	0·407
105·05	45·5	6·609	126·30	90·0	0·408
100·35	45·4	6·644	122·70	90·0	0·414
			100·00	90·0	0·454

* boiling point

Measurements have been made of the contraction resulting when sodium sulphate dissolves in water. This contraction, c, is given by $c = (v_1 + v_2) - v_3$ where v_1, v_2 and v_3 are the volumes of the solute, solvent and solution respectively.[45,46] The contraction increases with the concentration. The refractive index of aqueous saturated solutions of sodium sulphate[47] is given in Table XI.

Extension of the density determinations of saturated solutions of sodium sulphate to 100–450°C. were made by Benrath and co-workers,[48] and it was observed that dC/dt for solubility is the same for all greatly hydrated salts, but that in anhydrous and moderately hydrated salts dC/dt varies with C, the

TABLE XI.- PHYSICAL PROPERTIES OF SATURATED SOLUTIONS OF SODIUM SULPHATE

Temp. °C.	S.G.	n_D	Solubility	
			Molal concn.	%
15	1·1083	1·35077	0·907	11·62
20	1·1501	1·35646	1·297	16·02
25	1·2066	1·36380	1·846	21·73

solubility. For salts of this latter class dC/dt increases with ionic complexity and with water of crystallization.[49] Some experiments have been made[50] on the rate of solution of $Na_2SO_4,10H_2O$ in water, and of the solubility of iodine in solutions of sodium sulphate.[51]

The 'solubility' of sodium sulphate in superheated steam[52,53] at 500°C. is appreciable; see Table XII.

TABLE XII.- SOLUBILITY OF SODIUM SULPHATE IN HIGH-PRESSURE STEAM

Pressure (bars) at 500°C.	Solubility (wt.-% of Na_2SO_4)
67	0·0009
133	0·0037
666	0·0249
1000	0·431

The distribution coefficient between saturated aqueous and vapour phases is given as $K = (y'/y'')^n$, where y' and y'' are the phase densities and n is a constant for each substance; for sodium sulphate it is 8·4.

Anhydrous sodium sulphate was shown to be insoluble in liquid ammonia;[54] the solubility in ammonium sulphate solutions[55] and in aqueous ammonia solutions[56] is described (see page 1016) and studies have been made of the rates of absorption of carbon dioxide by ammonia/sodium sulphate solutions in comparison with ammonia/sodium chloride solutions.[57] The rates for these systems are similar (for identical concentrations) until sodium hydrogen carbonate begins to separate when the sodium chloride system accepts carbon dioxide much more rapidly than the sodium sulphate system.

The reciprocal influences of sodium and potassium sulphates on their solubility in water show that potassium sulphate is much more soluble in solutions of sodium sulphate than in water and this added solubility increases until the concentration of the latter is molar. Evidence of the double salt Na_2SO_4,K_2SO_4 exists.[58]

The solubility of iodine in sodium sulphate solutions does not increase with ionic strength according to the Debye–McAulay equation but at high concentrations ($\mu > 1{\cdot}6$) solubility increases faster than the equation would predict. This effect appears to be due to work done against interionic forces which is at first greater, and then less, than that required by theory. Some additional discrepancy may be due to the partial breakdown of the Debye–Hückel limiting law at high electrolyte concentrations.[59]

In molten $Na_2SO_4,10H_2O$ strong acids dissociate completely and acids of medium strength dissociate more than in water.[60]

Indelli[61] examined the conductivity and freezing point depression of aqueous solutions of sodium sulphate. The limiting values (at 25°C.) obtained were:-

Molality × 10^3	Conductivity × 10^4 (25°)
4·0489	9·212
274·38	373·23

Values for the 'integral heat of solution' (quantity of heat liberated by the solution of 1 mole of a substance in just enough solvent to give a saturated solution at a given temperature) for sodium sulphate in water, calculated according to a variety of formulae (van Deventer *et al.*,[62,63] Stackelberg[64] and Thomsen[65]) having proved unsatisfactory, Kompanskii[66] has proposed a new formula for computing the theoretical heat of solution.

Heats of dilution, molal heat contents and heat capacities of aqueous sodium sulphate solutions have been experimentally determined by Robinson and co-workers[67,68] and by Young *et al.*[70,71] mainly at 25°C. although some determinations have been made by the former workers at 15° and 20°C. Some of the results obtained are shown in Table XIII.

The expression $\Phi L_2 = f(m^{0\cdot5})$ was deduced from the values of the last three columns of Table XIII.

Further work on the heats of saturation and hydration of sodium sulphate[72,73] has shown that the heat of saturation of the hydrate, Qc, is given by:-

$$Qc = [T^2(1 - sC)d\log\left(\frac{p}{P}\right)]/503CdT,$$

where Qc is the heat of saturation of the hydrate Na_2SO_4,sH_2O, T the absolute temperature, and C the concentration of the saturated solution, P and p being the vapour pressure of water and the solution respectively. The analogous equation for the heat of hydration $X^{s_1}_{s_2}$ is:-

$$X^{s_1}_{s_2} = [T^2(s_1 - s_2)d\log\left(\frac{p}{P}\right)]/503dT.$$

Experimental and calculated values agree for Na_2SO_4,nH_2O for $n = s_1 = 10$ and $n = s_2 = 0$.

The heat of solution of magnesium sulphate heptahydrate in sodium sulphate solutions (ΔH g.-cal./mole) increases rapidly with increasing concentration of the sodium salt.[74] Figures are given in Tables XIV and XV.

TABLE XIV.- HEATS OF SOLUTION OF $MgSO_4,7H_2O$ IN SODIUM SULPHATE SOLUTIONS

Temp. °C.	$MgSO_4,7H_2O$ in H_2O Molality	ΔH	0·139 molar $MgSO_4,7H_2O$ in Na_2SO_4 of molality	ΔH
25	0·0	3080	0·0	3850
	0·110	3838	0·417	3860
	0·311	4078	0·914	3885
	0·643	4164	2·134	3900
	1·773	4428	2·787	3936
	2·230	4540	2·787	3936
35	0·114	3852	0·0	3852
	0·114		1·176	3990
	0·114		2·717	4120
45	0·111	3847	0·0	3858
	0·140	3860	0·828	4070
	0·248	4105	1·547	4295
	0·350	4160		4295

The water of hydration of sodium sulphate has been studied[75] by inoculating a saturated solution of sodium sulphate coloured with Bright Orange G, with a seed of $Na_2SO_4,10H_2O$. The crystals and mother-liquor were separated and the amount of dye in each determined, directly in the case of the mother-

TABLE XIII.- EXPERIMENTAL INTERMEDIATE HEATS AND APPARENT RELATIVE HEAT CONTENTS OF DILUTION OF AQUEOUS SODIUM SULPHATE SOLUTIONS

	m_1	$m_2 \times 10^3$	g.-cal.	ΔH g.-cal./mole Na_2SO_4	ΔH $(m_1 - m_2)$	ΦL_2 (m_2)	ΦL_2 (m_1)	Mean $L_2\,(m_1)$
15° C.	0·4014	2·692	+1·480± 0·01	+549·3± 3·6	+198·5	107·4	−91·1	−90·4
	0·4014	5·366	+1·570± 0·01	+566·5± 1·8	+230·7	141·1	−89·6	
	0·2006	1·351	+1·2556± 0·0016	+189·2± 1·2	−61·2	79·9	+141·1	+141·3
	0·2006	2·692	+0·2887± 0·0026	+204·0± 1·2	−34·2	107·4	141·6	
	0·1005	0·6778	−0·0065± 0·0006	−9·6± 0·9	−172·8	58·5	231·3	231·5
	0·1005	1·351	+0·0139± 0·0003	+5·5± 0·5	−159·7	79·9	231·6	
	0·05037	0·3401	−0·0313± 0·0004	−92·1± 1·2	−159·7	79·9	231·6	231·5
	0·05037	0·6778	−0·0256± 0·0003	−83·6± 1·2	−159·7	79·9	231·6	
	0·02525	0·1705	−0·0218± 0·0003	−127·9± 1·7	−159·7	79·9	231·6	231·5
	0·02525	0·3401	−0·0187± 0·0005	−118·6± 2·5	−159·7	79·9	231·6	
20° C.	0·4014	2·692	+1·023± 0·006	+380·2± 2·2	380·2	93·8	−286·4	−287·2
	0·4014	5·366	+1·177± 0·008	+408·8± 1·8	408·8	120·8	−288·0	
	0·2006	1·351	+0·0816± 0·0004	+60·4± 0·3	60·4	70·6	10·2	10·0
	0·2006	2·692	+0·1451± 0·0010	+84·0± 0·4	84·0	93·8	9·8	

25° C.	0·1005	0·6778	−0·0630± 0·0006	−92·9± 0·9	−92·9	52·1	145·0	145·6
	0·1005	1·351	−0·0396± 0·0007	−75·6± 0·7	−75·6	70·6	146·2	
	0·05037	0·3401	−0·0513± 0·0006	−151·0± 1·7	−151·0	37·9	188·9	188·6
	0·05037	0·6778	−0·0413± 0·0006	−136·2± 1·2	−136·2	52·1	188·3	
	0·02525	0·1705	−0·0283± 0·0003	−166·2± 1·9	−166·2	27·4	193·6	193·0
	0·02525	0·3401	−0·0243± 0·0006	−154·4± 2·2	−154·4	37·9	192·3	
	0·01267	0·0856	−0·0122± 0·0062	−142·8± 2·9	−142·8	19·7	162·5	163·6
	0·01267	0·1705	−0·0113± 0·0064	−137·2± 2·3	−137·3	27·4	164·7	
	0·4014	2·692	+0·5344± 0·0038	+198·5± 1·4	+549·6	71·9	−477·6	−477·6
	0·4014	5·366	+0·7072± 0·0065	+230·7± 1·4	+566·5	88·9	−477·6	
	0·2006	1·351	−0·0827± 0·0001	−61·2± 0·1	+189·2	55·4	−133·8	−133·0
	0·2006	2·692	−0·0095± 0·0024	−34·2± 0·9	+204·0	71·9	−132·1	
	0·1005	0·6778	−0·1171± 0·0012	−172·8± 1·8	−9·6	41·5	51·1	50·5
	0·1005	1·351	−0·0894± 0·0018	−150·7± 1·6	+5·5	55·4	49·9	
	0·05037	0·3041	−0·0894± 0·0018	−150·7± 1·6	−92·1	30·5	122·6	123·9
	0·05037	0·6778	−0·0894± 0·0018	−150·7± 1·6	−83·6	41·5	125·1	
	0·02525	0·1705	−0·0894± 0·0018	−150·7± 1·6	−127·9	22·2	150·1	149·6
	0·02525	0·3401	−0·0894± 0·0018	−150·7± 1·6	−118·6	30·5	149·1	

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TABLE XV.- VALUES OF TEMPERATURE COEFFICIENT OF HEAT OF SOLUTION FOR $MgSO_4$ (ANHYDROUS) IN AQUEOUS SODIUM SULPHATE

Temp. °C.	0·252 Molal $MgSO_4$ Molality of Na_2SO_4	ΔH
25	0·00	−20873
	14·16	−20835
	27·85	−20772
35	0·00	−21495
	27·85	−21228
45	0·00	−22146
	27·85	−21693

liquor and by solution of the crystals in water. The value of n in Na_2SO_4, $n H_2O$ was determined as 10·3. From vapour pressure determinations[76] of sodium sulphate at various concentrations the limit heats of solution were calculated as −16·80 and −13·78 g.-cal. at 20°C.; direct determinations gave −16·60 and −13·96 g.-cal. Tursi and Thompson[77] examined the effect of dissolved sodium sulphate in the vapour-liquid equilibrium of the water-ethanol system. Further supporting results[78] were obtained pycnometrically (density) and by Pearce and Snow's method[79] (vapour pressure).

The volatility of sodium sulphate itself was examined in connexion with the loss of alkali from the smelting furnaces of sulphite-paper plants;[80] the relation

$$\log p(\text{mm.Hg}) = -(7230/T) + 4{\cdot}42$$

was established.

The melting point of sodium sulphate was obtained by observing the conductivity change with temperature in supersaturated solutions; a sharp break at 33°C. was shown at all concentrations.[81]

Using a diaphragm cell technique the self-diffusion coefficients for the diffusion of the Na^+ and SO_4^{--} ions in solutions of sodium sulphate were determined. The results are summarized in Table XVI, and do not vary greatly from the expected values.[82] The effect of pressure on the diffusion of the Na^+ and SO_4^{--} ions in water solutions has been examined; in general pressure tends to break down the structure, with a consequent increase in diffusion speed.[83] Figures for diffusion of Na^+ and SO_4^{--} at 20°C. (Na^+, D = 0·622 at 2 N; 0·684 at 1 N; 0·746 at 0·5 N; 0·782 at 0·25 N. and 0·800 at 0·1 N.) are comparable with those of Table XVI allowing for the temperature difference.[84]

TABLE XVI.- SELF-DIFFUSION COEFFICIENTS D(cm.^{2}/day) OF THE IONS IN SODIUM SULPHATE SOLUTION AT 25°C.

Concn. (eq./l.)	D Na^+	D SO_4^{--}
0·000	1·154	0·919
0·01	1·125 ± 0·8%	0·83 ± 1·0%
0·02	1·12 ± 0·0	
0·03		0·75 ± 0·4%
0·05	1·095 ± 0·6%	0·72 ± 0·7%
0·1		0·65
0·2	1·05 ± 0·0	0·61 ± 0·3%
0·4	1·00 ± 0·5%	0·57 ± 0·4%
0·55		0·57
0·7	0·935 ± 0·3%	0·555 ± 0·6%
1·2	0·845 ± 0·8%	0·53 ± 0·0

continued on following page

TABLE XVI.- continued

Concn. (eq./l.)	D Na$^+$	D SO$_4^{--}$
1·5	0·80 ± 0·5%	0·50
2·0	0·77 ± 0·4%	0·525 ± 0·4%
3·0	0·73 ± 1·2%	0·54 ± 0·6%

The difference in diffusion speeds of the ions Na$^+$ and SO$_4^{--}$ is further shown by the behaviour of sodium sulphate solutions undergoing dialysis, when the liquid passing through the diaphragm is alkaline and the residue acid.[85] Attempts to use this procedure for the removal of Na$^+$ ion from viscose waste proved unsatisfactory even using electrodialysis with antimonial lead anodes and iron cathodes.[86]

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Electrochemical

The electrical conductivity of sodium sulphate solutions has been widely studied; at low dilution (0·0005 N.) by Clews[1] who found no agreement between his results and those predicted by the Debye-Hückel and Onsager theories. Tables have been published[2] for the conductivity of aqueous solutions of sodium sulphate between 0·001 N. and 0·1 N. and between 18° and 85°C. The conductivity is quite different with high frequency currents.[3] The Soret

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coefficient for sodium sulphate[4] (2·8 ± 0·3) is in fair agreement with figures obtained by the addition of Soret coefficients of the ions. The heat of transference has been calculated as 0·7 kg.-cal./mole. Conductivities of sodium sulphate at concentrations 0·1 to 1 N. have also been measured[5] by a method in which a special design gives cells having a capacity independent of the nature of the electrolyte.

The effect of sodium sulphate on other electrolytes has been studied for many systems. Sucrose[6] enhances the conductivity of sodium sulphate according to the expression $\lambda = \lambda_\infty - a\sqrt{c}$ (Debye–Hückel). The increased solubility of boric acid[7] in sodium sulphate solutions is accompanied by a change in conductivity, and the effect of the presence of sodium sulphate in the $Pt,O_2/Na_2SO_4{-}Na_2CO_3{-}CO_2/Na_2SO_4{-}Na_2CO_3{-}CO_2/O_2Pt$ cell is to stabilize the e.m.f. set up by different concentrations of sodium carbonate so that the relation $E = (RT/2F)\log(N_2/N_1)$ holds (where N_1 and N_2 are mole-% of sodium carbonate).[8] The effect of sodium sulphate on the quenching of fluorescence of quinine^{++} ion by Br^- and of fluorescein^{--} by I^- has been studied.[9] It has been shown that there is a relation between the conductivity and viscosity of sodium sulphate solutions.[10] It is stated that by the discharge electrolysis of solutions containing cobalt and sodium sulphates the compounds $Na_2SO_4,10Co(OH)_2$ and $Na_2SO_4,15Co(OH)_2$ can be prepared.[11] On the other hand, sodium sulphate does not disturb[12] the equilibria:

$$CO_3^{--} + H_2O \rightleftharpoons HCO_3^- + OH^-$$
$$2HPO_4^{--} \rightleftharpoons H_2PO_4^- + PO_4^{---}$$

The decomposition voltage for $Na_2SO_4 + H_2O \rightarrow NaOH + H_2SO_4$ is 2·23 V. Sodium sulphate smooths the rate of deposition of zirconium in plating and secures a bright deposit.[13] The transference numbers were investigated by Longsworth[14] and interesting results were obtained by Gillet[15] by electrolysing cylindrical gels containing 3% sodium sulphate and 10% gelatin. By stopping the current and sectioning the gel information on the ionic state was obtained. On account of its great stability, a sodium sulphate–sulphuric acid solution has been recommended as a standard of conductivity.[16] Work on the influence of sodium sulphate on other electrolytes shows it to have a potential-reducing action; a typical[17] example is the application of 3×10^{-6} amp./sq.cm. to a platinum cathode in 0·2 N. copper sulphate solution at 18°C. Without sodium sulphate the potential of the cathode relative to a copper reference electrode is +15 mV.; with 0·2 N. sodium sulphate added this falls to +10 mV. The hydrogen overvoltage at a lead cathode is raised by sodium sulphate; advantage is taken of this by adding sodium sulphate to oxalic acid solutions being electrolytically reduced to glyoxylic acid, the yield being substantially increased.[18]

The conductivity of sodium sulphate has been used[19] to investigate the existence of compounds in the systems $Na_2SO_4{-}K_2SO_4{-}H_2O$ and $Na_2SO_4{-}MgSO_4{-}H_2O$. Small deviations were observed from the expected values at equimolecular proportions of the two salt-pairs. Several studies have been made of the anodic effect of sodium sulphate: in the passivation of iron,[20] with iron-chromium alloy anodes,[21] and with both pure and industrial aluminium;[22] there seems to be very little effect in either case.

Electrolysis of sodium sulphate – particularly of wastes containing this salt – has been studied as a means of industrially regenerating caustic soda and sulphuric acid.[23] Electrodialysis[24] of sodium sulphate solutions at 30°C. gives caustic soda and sulphuric acid recovery of moderate yields, but the process appears unsuitable for large scale use and at best yields only dilute acid. Stender and Seerak[25] designed and operated pilot plant for converting sodium sulphate to caustic soda and sulphuric acid. Using cells with argentiferous lead anodes and a mercury cathode they obtained a fair yield of caustic

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soda, and used the cycle shown in Fig. 21 for recovery of acid and excess sodium sulphate.

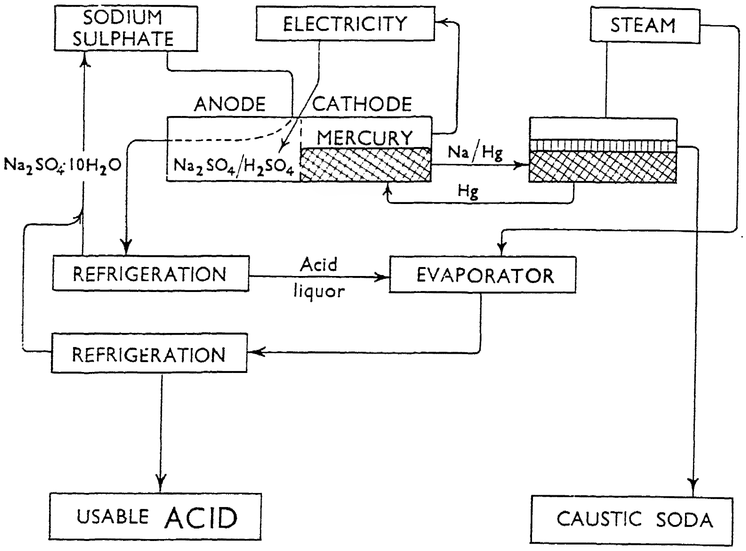

FIG. 21.- PROCESS OF THE ELECTROLYTIC PRODUCTION OF SODA FOR Na_2SO_4.

The difficulties of construction of a suitable cell diaphragm and the high electrical energy utilization figures contribute to make this process uneconomic. The best concentrations produced by such cells appears to be 0·18% sodium in mercury, and 0·53 mole/l. of sulphuric acid (before concentration).

Electrolysis of molten sodium sulphate[26] using magnetite electrodes leads to a mixture of sulphur dioxide, sulphur trioxide and oxygen at the anode and sodium oxide, Na_2O, at the cathode where, however, it combines with the cathode to give sodium ferrite, $NaFeO_2$.

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CHEMICAL PROPERTIES OF SODIUM SULPHATE

When heated alone sodium sulphate volatilizes leaving only a small alkaline residue, (Mellor, II, 672), but in the presence of a variety of catalysts a mixture of sulphur dioxide, sulphur trioxide and oxygen is evolved and a residue relatively rich in sodium oxide remains. The oxides[1, 2] of vanadium, tungsten, chromium, cerium, iron and silicon lead to catalytic decomposition at 1200°C. in that order of effectiveness, maximum decomposition being 8·4% with vanadium pentoxide. Mixtures of the other oxides with silica have a more powerful catalytic action, and the order of effectiveness is altered to Fe_2O_3, 17·15% (decomposition after 1 hr.); V_2O_5, 16·12; WO_3, 12·58; CeO_2, 12·46, and Cr_2O_3, 7·18. It is noteworthy that ferric oxide has no effect on the decomposition in the absence of silica.

It has been shown that[3] the decomposition of silica/sodium sulphate mixtures starts at 1100°C. and that the velocity of reaction at higher temperatures is related to the degree of dispersion of the silica. The catalytic effect is even greater with kaolin but is quite small with washed river sand. The presence of silica or kaolin in stoicheiometrical proportions leads to complete reaction, the products being sulphur dioxide (with some trioxide), sodium silicate and aluminate.

The presence of carbon[4] in mixtures of sodium sulphate and kaolin leads to more rapid reaction at lower temperatures. After 1 hr. at 1050°C. in mixtures containing equimolar proportions of charcoal and sodium sulphate with excess of kaolin (6 mols. calculated as $Al_2O_3 + SiO_2$) 98% of the sulphate was decomposed. The carbon also ensures that the sulphur dioxide evolved is free from trioxide.[5–7]

Sodium sulphate and alumina react at 1100–1300°C. yielding sulphur dioxide and trioxide with some oxygen. The mixture loses[8] about 10% of its weight after heating for 1 hr. at 1280°C. In an attempt to elucidate the course of this reaction Lileev and Rozentreter studied the decomposition of equimolar mixtures of alumina and sodium sulphate at 1200–1300°C. in air and in nitrogen and of alumina and sodium sulphide at 960–1000°C. in air, and also in nitrogen and in the presence of carbon. They concluded that sodium aluminate (leading on acidification to soluble aluminium salts) is formed directly from alumina and sodium sulphate, but not from alumina and sodium sulphide, and that reducing conditions were not conducive to high yields of aluminate.[9] Related to this is the observation[10] that soda-glass heated to 600°C. in sulphur dioxide shows a considerable increase in surface hardness. The glass also shows, after heating, a thin white layer on the surface which proves to be sodium sulphate and represents a surface loss of sodium oxide.

Sodium sulphate reacts with hydrogen[11] even at 800°C. At first, sulphite is formed but at higher temperatures the sulphur is removed as hydrogen sulphide and sodium hydroxide remains; however this reaction is never complete.

The reduction of sodium sulphate by hydrogen under pressure[12] proceeds directly and completely to the sulphide in the presence of iron powder at 600–

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650°C., and similar results are obtained with methane above 800°C. In general, however, the temperature of 650°C. should not be exceeded because of the eutectic at 665°C. in the Na_2SO_4-Na_2S system.

With aluminium powder, sodium sulphate can react explosively.[13] Two reactions are involved:-

$$8Al + 3Na_2SO_4 \rightarrow 4Al_2O_3 + 3Na_2S$$
$$8Al + 3Na_2SO_4 \rightarrow 3Al_2O_3 + 3Na_2O + Al_2S_3$$

Both reactions are strongly exothermic.

Sodium sulphate increases the time of the iodine clock reaction[14] and reacts with fluorine[15] according to the reaction:-

$$2F_2 + Na_2SO_4 \rightarrow 2NaF + SO_2F_2 + O_2$$

After two minutes at 100°C. the reaction is only 2% complete; at 200°C. it is 20% and at 300°C. 40% complete in the same time. With sodium sulphite a preliminary reaction:

$$2F_2 + 2Na_2SO_3 \rightarrow Na_2SO_4 + SO_2F_2 + 2NaF$$

takes place, followed by the previous reaction. Boron trifluoride forms[16] a complex with sodium sulphate, Na_2SO_4,BF_3.

A reaction occurs[17] between oxalic acid and sodium sulphate:-

$$Na_2SO_4,10H_2O + H_2C_2O_4,2H_2O \rightarrow NaHC_2O_4,H_2O + NaHSO_4 + 11H_2O$$

The sodium hydrogen oxalate separates out almost quantitatively if the solution is made acid with sulphuric acid.

The presence of sodium sulphate leads to a sharp increase in water-soluble P_2O_5 derivable from tricalcium phosphate.[18] At high temperatures and pressures calcium phosphate, $Ca_3(PO_4)_2$, and sodium sulphate react to give partial conversion to calcium sulphate and sodium phosphate.[19] The degree of conversion depends to some extent on the physical condition of the calcium phosphate; bone meal gives a 77% conversion at 100°C., whilst phosphorite is only 67% decomposed at 200°C.

Ammonia and sodium sulphate react slowly at 720°C. or more rapidly at 800–1000°C., affording products similar to those obtained from sodium sulphate and hydrogen.[20]

The oxidation of sodium sulphate electrolytically will be discussed in a subsequent Supplement under the formation of per-salts of the sulphuric acid series.

It has been shown that sodium sulphate assists in protecting ingot iron from attack by caustic alkalies. With 0·01–0·9 mol. per l. the corrosion by 0·02 N. sodium hydroxide becomes less than that for pure water.[21]

Many detailed studies have been made of the effect of sodium sulphate – molten, in vapour phase and in aqueous solution – on refractories and cements. The molten material induces a rapid deterioration of both clay and alumina refractories,[22, 23] and the effect of the vapour is well marked at temperatures of 1200°C.[24] There is no doubt that aqueous sodium sulphate not only leads to loss of strength in the hardening of Portland cements but such solutions progressively weaken such cement when it has already hardened.[25–31] Samples of cement/sand mortars normally mixed and hardened, when boiled for 4 hr. in saturated sodium sulphate and dried at 150°C., completely disintegrated after seven cycles.[32] The addition of up to 15% of natural burnt clay is said to prevent the deterioration due to dilute sodium sulphate solutions.[33–35] The presence of Na_2O and/or K_2O in the kiln during the production of Portland cement can lead to sulphates in the clinker with deleterious effect on the final strength of the mixes.[36] It appears that the reaction involved in the weakening of cement by alkali metal sulphates is $Na_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2NaOH$.[37]

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The study of pure calcium monoaluminate and calcium β-orthosilicate cements with sand shows a similar deterioration in the presence of sodium sulphate.[38,39] Building stones (sandstone, limestone, marble, granite, gneiss) and even brickwork are weakened and ultimately destroyed structurally by prolonged exposure to sodium sulphate solutions.[40-42]

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USES

The two main uses of sodium sulphate are in the production of alkali and glass; it also finds considerable use in paper making and textile dyeing.

Alkali Manufacture

The production of sodium carbonate and bicarbonate from salt and salt-cake is dealt with elsewhere (see page 1065); this section is confined to attempts to obtain industrial yields of alkali directly from sodium sulphate. The causticising of sodium sulphate with lime[1] gives poor yields of sodium hydroxide; better yields are obtained with baryta, but the process is uneconomic. Where large supplies of mirabilite or other sodium sulphate minerals or brines are available the production of a 'sulphate' soda-ash is now common. Belopol'skii in 1940, after several years of laboratory work,[2] showed that the large scale conversion of sodium sulphate to bicarbonate and carbonate could be carried out in the conventional Solvay plant.[3–5] After calcination, the bicarbonate gave a soda-ash of 97·6% purity. The other product is ammonium sulphate. Desai[6] has shown that the optimum mol. ratio of NH_3:CO_2:Na_2SO_4 is 1:1:1 with the sodium sulphate as a saturated solution at 34°C. A Japanese process[8] describes the starting point as recovered liquor from a previous batch, in which each kilogram of water has dissolved in it 155 g. Na_2SO_4, 250 g. $(NH_4)_2SO_4$, and 140 g. NH_4HCO_3. This liquor is treated with fresh sodium sulphate (500 g.), water (120 g.), and ammonia (30 g.) and cooled to 19·5°C. when 600 g. of sodium ammonium sulphate, $Na_2SO_4,(NH_4)_2SO_4,4H_2O$, separates. The filtrate from this is carbonated, when sodium bicarbonate is precipitated. This is filtered from the liquor which is then recycled. Brines containing both chloride and sulphate have been used in the ammonia-soda process.[7]

Various cells for the preparation of caustic alkali and sulphuric acid from sodium sulphate have been described.[9–17] The majority are based in design on chloride cells and use a moving stream of mercury as cathode and lead or lead/silver anodes. A comparison of mercury and diaphragm cells[18] shows the former to be more satisfactory, producing a purer sodium hydroxide with lower current consumption. Sulphate cells have several disadvantages, not the least of which are (*a*) that the current consumption per ton of alkali produced is some 20% higher than that required to produce the same quantity from sodium chloride, and (*b*) the sulphuric acid produced is dilute and associated with unchanged sodium sulphate, making it difficult to concentrate and purify. Where, however, as in the rayon industry the spinning bath is based on a moderately dilute aqueous solution of sulphuric acid and sodium hydrogen sulphate, the process appears attractive. The process has only been able in any way to compete with the traditional chlorine-caustic process where immediate access to high grade mineral sodium sulphate and considerable distance from rock-salt obtains. Attempts have been made[19] to use a hydrated tungstic acid as a catalyst to promote the anodic oxidation of sulphur dioxide introduced into the anode section of sulphate cells; to use moving streams of copper amalgam as cathode and bismuth amalgam as anode,[20] and to recover the sulphate from the anode liquor of sulphate cells by circulation through a cation-absorbing exchange resin. Recovery of the acid is made by continual circulation of hot ammonia/ammonium sulphate liquor through the acid-saturated resin until ammonium sulphate begins to crystallize; the liquor is then cooled, filtered from ammonium sulphate crystals and returned with fresh ammonia to the recovery circulation.[21] None of these processes appears to have been widely used.

Various processes have been described for using sodium sulphate as a source of alkali by decomposing it thermally. Briquettes are made of hydrated sodium sulphate and a supporting material; these when heated in a vacuum at 1100–1200°C. decompose with the formation of sodium oxide and sulphur trioxide which condenses with the water of hydration and so forms sulphuric acid. The briquettes on leaching with hot water give a strong solution of sodium hydroxide, but do not lose their shape, and may be reimpregnated with sodium sulphate and used repeatedly.[22]

If sodium sulphate is heated in a current of semi-water gas a yield of about 93% of sodium carbonate is obtained at 630°C. and $\frac{1}{4}$ atm. The semi-producer gas should be adjusted in composition so that the concentration of carbon monoxide and hydrogen is volumetrically equal and these two gases form 35% of the total gas.[23,24] A variant of this method[25] is to atomize melted sodium sulphate into an atmosphere of steam and carbon dioxide at 1000–1500°C. Yet another variation is to blow semi-water gas into molten sodium sulphate;[26] this is, of course, coming close to the reduction[27] of sulphate to sulphide with carbon which was the basis of the LeBlanc process.

Several attempts have been made[28–30] to combine alkali manufacture with sulphur trioxide recovery by using electric furnaces to avoid diluting the gases.

Sodium Sulphate in Glass Making

The use of sodium sulphate in glass-making was well known in early times, and Laksman made special glass furnaces to utilise sodium sulphate in 1784.[31] Much of the early investigation on the theory of the use of sodium sulphate is due to Fourcault[32] who worked out the standard batch compositions which have been regularly used since 1920. Two main reasons have led to the use of sodium sulphate in glass making. The first is that small amounts of sodium sulphate have a beneficial effect on the rate of melting and the elimination of alkaline bubbles and 'seed';[33–35] the second is that native sodium sulphate (if within certain fairly wide limits of purity)[36] is often available in districts where soda ash is expensive, so that sodium sulphate offers a cheap alternative source of the Na_2O of the glass system.[37–44]

The reactions taking place in the melt owing to the presence of sodium sulphate are complex;[45–48] a reduction to sodium sulphite is an essential stage as the sulphite not only disproportionates to sulphate and sulphide, $4Na_2SO_3 \rightarrow 3Na_2SO_4 + Na_2S$, but also decomposes to sodium oxide and sulphur dioxide. A reducing agent in the mix facilitates the absorption of sodium sulphate into the glass system by increasing the rapidity of formation of sodium sulphite. Coal, charcoal and graphite dust have been used as reducing agents[49–56] according to the quality of the glass required.

While the use of sodium sulphate improves the boiling and working properties of glasses of high silica content[57] there are several disadvantages. In the first place all the sulphur of the sulphate (apart from that skimmed off as "glass-gall") is converted to sulphur dioxide containing a little trioxide which must be recovered in all but the smallest operations. The dilution of these gases with the furnace gases usually means that the exit gas from lehrs contains not more than a few per cent. of sulphur dioxide, the recovery of which, at this dilution, is a difficult problem.

Secondly, the corrosive action on the refractory pots ("monkey pots") is much higher than with glass prepared without sodium sulphate. This not only adds to the cost, but also discolours the glass since the sulphate tends to extract iron oxide. Thirdly, the complex reactions taking place in the oxidative and reductive reactions leading to sodium oxide and sulphide leave the oxide of iron as ferric oxide rather than ferrous oxide, thereby increasing the colour and necessitating the use of more 'bleacher' (manganese oxide or selenium). If the iron is in considerable quantity (0·7–0·8%) it is possible[58] to obtain good blue and green glasses by working the furnace with gases containing 9–12% of carbon monoxide.

The use of sodium sulphate in mechanized continuous melting furnaces is difficult; the main economic factor in such plant is the length of the continuous run, that is, the time elapsing between starting up the furnace and shutting down for relining the tank. Any batch alteration which increases the wear on the refractories is, therefore, undesirable.[59–63] The sodium sulphate used for glass-making is usually dehydrated, dried, and ground in a preliminary plant.[64,65]

Other Uses

The use of sodium sulphate in paper pulp production depends on the fact that sulphur dioxide and sodium sulphate can replace lime and bisulphite liquor in the cooking of chips. Since sulphur dioxide is recovered as a by-product in paper-making, the process is economically attractive.[66–71]

In dyeing, sodium sulphate is a useful 'leveller'[72,73] and has the advantage that, unlike acid levellers, it has no effect on stainless steel equipment.[74] It is held[75,76] that the mechanism of levelling is that the sodium sulphate induces the solution of dye from the more heavily dyed portions and its redeposition on parts less heavily dyed.

Sodium sulphate accelerates the setting of plaster of Paris;[77] the strength of the dried plaster is somewhat lower[78] and more than 0·5% of sodium sulphate may cause efflorescence.[79] This tendency to efflorescence has been observed in latex paints containing sodium sulphate; it can be controlled[80] by adding potassium polyphosphate, $K_3P_3O_{10}$, so that the K:Na ratio is at least 3:1.

The hardening of Portland cement is also accelerated by sodium sulphate,[81] especially cements of the pozzolanic type. There appears to be no loss of strength;[82] on the contrary, the presence of sodium sulphate appears to augment the retardation of setting induced by carboxymethylcellulose[83] in slurries used for high temperature deep oil wells. Sodium sulphate has been used for the production of a cement by firing it with coal ash, limestone and coal.[84] Portland cement is very easily attacked by dilute sodium sulphate solutions; where floors are likely to be subjected to the continual action of such solutions it is desirable to use a special cement prepared by grinding 2 parts of ordinary Portland cement clinker with 1 part of a clinker obtained by calcining kaolinite clay at 700–800°C. for 12 hr.; in addition 3% of gypsum is used. This is a cement which in strength and hardening properties differs little from ordinary Portland cement but is almost unaffected by dilute sodium sulphate solutions.[85]

Attempts have been made to use sodium sulphate in the decomposition of rock-phosphate ($CaPO_4$), soluble sodium phosphate and calcium sulphate being obtained. The latter can be dehydrated for plaster and the former used as such or converted to phosphoric acid.[86–89] It is remarkable that sodium sulphate greatly increases the yield of carbon disulphide from carbon and sulphur.[90]

Among the miscellaneous uses of sodium sulphate may be mentioned thermometry, as a standardizing substance;[91] as a dehydrating or concentrating agent;[92,93] in organic chemistry as a promoter, especially in benzene sulphonation[94] and *cis*-butene oxidation;[95] in metallurgy for assisting in refining mattes[96] and for metal surface treatment;[97,98] as a reagent for regenerating ion-exchange resins[99] and for the production of safety explosives.[100]

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BIOLOGICAL PROPERTIES OF SODIUM SULPHATE

The principal effect of sodium sulphate is the stimulation of diuresis, for which property it was valued by the early chemists. This diuresis is increased by traces of strontium ion,[1] and can be induced both by oral and intravenous administration.[2] Much of the sodium sulphate is retained.[3,4] The diuresis persists even in animals made nephritic with cantharidin,[5] and with the aglomerular kidney[6] (with which theophylline shows only a very slight diuresis). The relation between the diuretic action of sodium sulphate and the energy consumption of the kidney has shown that the compound has little effect on the normal energy relations; sodium chloride, on the other hand, induces a 200–300% increase in oxygen uptake.[7] The intravenous injection of comparatively small doses of 20–30% sodium sulphate is fatal to rabbits.[8,9] Sodium sulphate also increases the flow of bile.[10]

The cathartic action of sodium sulphate[11] and its absorption from intestinal loops[12,13] are slight; sodium sulphate has practically no influence on many enzyme actions[14] but retards the growth of *Salmonella* and *Shigella*.[15]

Sodium sulphate is used as an antidote in barium poisoning[16,17] and has shown a reflex respiratory stimulating action.[18] The metabolism of sodium sulphate has been studied by Sato[19] in rabbits under normal and abnormal conditions. Sodium sulphate has a protective action on the snail heart towards low temperature stoppage.[20]

In the vegetable kingdom the main activity of sodium sulphate is to increase the weight-yield of root crops, notably sugar beet.[21] In general, plants seem slightly more sensitive to excessive soil sodium sulphate than to sodium chloride.[22–24]

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SODIUM HYDROGEN SULPHATE

In general sodium hydrogen sulphate is prepared industrially by modifications of processes designed to produce sodium sulphate, using twice the amount of sulphuric acid. This process is an integral part of the old Leblanc method of salt-cake manufacture in which sodium chloride and sulphuric acid in equimolecular proportions give hydrogen chloride and sodium hydrogen sulphate. The process has been made continuous by the use of a ferrosilicon drum heated electrically.[1,2]

Some sodium hydrogen sulphate is recovered from wastes; nitre cake is recovered by heating with sulphuric acid to 150°C. and granulating the product;[3] rayon spinning bath waste is regenerated by adding sulphuric acid and crystallizing out sodium hydrogen sulphate;[4,5] the residual liquor can be re-used in the spinning bath. Recovery of sodium hydrogen sulphate from fluxing operations is an important economic step in ore treatment.[6] The product of many of these recovery and production processes is molten sodium hydrogen sulphate; a common procedure is to granulate this, or convert it to spherical pellets.[7–9]

Physical Properties

The vapour pressures of sodium hydrogen sulphate have been widely examined,[10] and results of this work are shown in Tables XVII and XVIII. Gibson has determined the fictive volumes of sodium sulphate in sulphuric acid solution which demonstrates the formation of sodium hydrogen sulphate[11] in solution.

TABLE XVII.-ISOPIESTIC SOLUTIONS OF $NaHSO_4$ AND NaCl (25°C.).

m_{NaHSO_4}	m_{NaCl}	$m_{H_2SO_4}$	m_{NaCl}	m $NaHSO_4$	m NaCl
0·1041	0·1190	1·084	1·119	4·191	4·265
0·1237	0·1400	1·174	1·210	5·112	5·122
0·1482	0·1664	1·340	1·376	5·240	5·228
0·1529	0·1713	1·382	1·420	5·610	5·555
0·2039	0·2255	1·632	1·671	6·320	6·147
0·2823	0·3078	2·398	2·456		
0·4272	0·4573	3·065	3·138		
0·6425	0·6763	4·067	4·140		
0·7774	0·8119				

The hydrolysis constant for sodium hydrogen sulphate, which may be regarded as an acid, is the same as the dissociation constant;[12] in the dilution range 1 to 1000 the degree of dissociation varied from 0·316 to 0·851. Rudolphi's formula,[13] $K = x^2/(1 - x)v$, gave a fairly constant value of 0·146. Other conductivity studies have given the relation between sodium hydrogen sulphate and the conductivity of sulphuric acid.[14,15]

TABLE XVIII.- RELATIVE MOLAL VAPOUR PRESSURE LOWERINGS, $(p_0-p)/mp_0$, OF $NaHSO_4$ AND $KHSO_4$ AT 25°C., RELATIVE TO p_1 = 23·756 mm.

m	$NaHSO_4$	$KHSO_4$	m	$NaHSO_4$	$KHSO_4$
0·1	0·03838	0·03775	1·2	0·03425	0·03074
0·125	0·03778	0·03722	1·4	0·03435	0·03035
0·15	0·03737	0·03669	1·6	0·03456	0·03000
0·2	0·03671	0·03589	1·8	0·03482	0·02977
0·3	0·03590	0·03469	2·0	0·03508	0·02957
0·4	0·03537	0·03384	2·5	0·03582	0·02916
0·5	0·03502	0·03316	3·0	0·03658	
0·6	0·03477	0·03266	3·5	0·03731	
0·7	0·03460	0·03223	4·0	0·03795	

continued on following page

TABLE XVIII.- continued

m	$NaHSO_4$	$KHSO_4$	*m*	$NaHSO_4$	$KHSO_4$
0·8	0·03445	0·03188	4·5	0·03847	
0·9	0·03436	0·03156	5·0	0·03882	
1·0	0·03432	0·03129	6·0	0·03	

Saturated aqueous sodium hydrogen sulphate has been recommended as a suitable fluid in gas-analysis apparatus for confining gases for measurement.[16] The solubilities of gases in such solutions are given in Table XIX.

TABLE XIX.-SOLUBILITIES OF GASES IN SATURATED $NaHSO_4$ SOLUTION

Gas	*Q* = (amt. in ml. dissolved in 1 ml. solution)	Gas	*Q*
SO_2	13·6	C_2H_6	0·0108
CO_2	0·27	H_2	0·0073
N_2O	0·16	CO	0·0039
C_2H_2	0·34	O_2	0·0089
C_2H_4	0·024	N_2	0·0049
CH_4	0·0093		

Chemical Properties

The thermal dissociation of sodium hydrogen sulphate proceeds by the following stages.[17] If heated at 240–250°C. for a long period it produces pure $Na_2S_2O_7$ which above 300°C. decomposes slowly; at 400°C. the decomposition is very rapid. The thermal decomposition of sodium hydrogen sulphate between 130 and 180°C. is represented by the equation:-

$$\log p_{\mathrm{mm}} = -(4298{\cdot}88/T) + 10{\cdot}7458$$

The solidification point of sodium hydrogen sulphate is 182°C., and the dissociation pressure of the system is given in Table XX.

TABLE XX.- DISSOCIATION PRESSURE (mm.) OF THE SYSTEM $2NaHSO_{4(\mathrm{liq.})} \rightleftharpoons Na_2S_2O_{7(\mathrm{s})} + H_2O_{(\mathrm{g})}$

T°	Pressure (mm.)	*T*°	Pressure (mm.)
185	21·8	240	58·1
195	27·1	260	68·6
205	32·8	280	77·2
220	42·6		

Sodium hydrogen sulphate reacts with hydrogen chloride only in the presence of traces of water.[18] When sodium hydrogen sulphate and disodium hydrogen phosphate are heated[19] together, a disproportionation reaction takes place giving sodium sulphate and sodium dihydrogen phosphate. Molten sodium hydrogen sulphate dissolves metals such as titanium, vanadium and zirconium very rapidly.[20]

The catalytic activity of sodium hydrogen sulphate is marked, especially in dehydrations. The alkanols can give either ethers or alkenes on catalytic dehydration with sodium hydrogen sulphate,[21] the tendency towards alkene formation being more marked in the vapour phase.[22] Hydroaromatic alcohols are similarly dehydrated, for example *cyclo*hexanol gives *cyclo*hexene;[23] and the method has been applied to the dehydration of castor oil to produce a drying oil for paint manufacture.[24–26]

Aromatic' alcohols, such as benzyl alcohol, give high yields of ethers when dehydrated with sodium hydrogen sulphate.[27] Senderens[28,29] has studied the variation of dehydrative catalytic activity with sodium content between H_2SO_4 and Na_2SO_4, finding that for ether formation the values differ little between H_2SO_4 and $NaHSO_4$ (although degradative by-products are less with the latter) but fall off rapidly as the composition Na_2SO_4 is approached.

Uses of Sodium Hydrogen Sulphate

The accumulation of by-product sodium hydrogen sulphate has led to its being used as a source of sulphuric acid. When it is distilled with sand, sulphuric acid is given off.[30] It may also be used to decompose rock-phosphate, giving soluble acid calcium phosphates.[31–33] An ion-exchange resin system has been evolved to give neutral sodium sulphate and a resin/sulphuric acid complex from sodium hydrogen sulphate;[34] the resin/acid complex is treated with ammonia to form ammonium sulphate solution and regenerated resin.

Other proposals include the calcination of a 50% magma of sodium hydrogen sulphate and water with sawdust in closed retorts; sodium sulphide and active carbon are produced.[35] Tasaki[36] takes the process a stage farther and treats the sulphide liquor with waste gases containing sulphur dioxide to obtain precipitated sulphur.

In glass making[37] sodium hydrogen sulphate is less valuable than the neutral sulphate; more silica separates during melting and the glass shows haze. The use of sodium hydrogen sulphate as a promoter in the hardening of gypsum or anhydrite cements[38,39] offers little if any advantage over the neutral sulphate. The acid sulphate is widely used in the making of soluble starch.[40]

Among the miscellaneous uses of sodium hydrogen sulphate may be mentioned those as a soil disinfectant against *Salmonella pullorum* in poultry yards;[41] in acid hardening-fixing baths for photographic films;[42] as a heat treatment bath for aluminium alloys up to 950°C. in conjunction with sodium nitrate;[43] in the molten form as a pre-treatment before chromium plating to ensure adherence of the film;[44] and in dyeing.[45]

The existence of a sulphate $Na_3H(SO_4)_2$ has been demonstrated (see page 1012). It forms glossy needles on cooling a solution of sodium sulphate in dilute sulphuric acid.[46] The crystals are strongly birefringent, n = 1·459, n = 1·479 ± 0·004. It has been used as a sulphonating agent in organic syntheses.[47]

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SECTION XXXVI

SODIUM CARBONATE

By C. R. BAILEY

OCCURRENCE AND EXTRACTION

Since the First World War there has been continuous geological and chemical exploration of natural waters and salt deposits for their carbonate and bicarbonate content. The following account supplements Mellor II, and material available there is not repeated unless demanded by the context.

OCCURRENCE

Mineral soda is found principally as (i) the decahydrate, *sal soda* or *natron*, (ii) the monohydrate or *thermonatrite*, (iii) *nahcolite* ($NaHCO_3$), (iv) the sesquicarbonate, *trona* or *urao*, (v) *gaylussite* ($Na_2CO_3,CaCO_3,5H_2O$), (vi) *burkeite* ($Na_2CO_3,2Na_2SO_4$), (vii) *pirssonite* ($Na_2CO_3,CaCO_3,2H_2O$), (viii) *northupite* ($Na_2CO_3,MgCO_3,NaCl$), (ix) *tychite* ($2Na_2CO_3,2MgCO_3,Na_2SO_4$), (x) *hanksite* ($2Na_2CO_3,9Na_2SO_4,KCl$), (xi) *dawsonite* ($Na_3Al(CO_3)_3,2Al(OH)_3$), and (xii) *shortite* ($Na_2CO_3,2CaCO_3$). There are several general accounts of the natural sources of soda.[1,2]

The topography and geochemistry of soda lakes are much the same in all parts of the world. They generally occur near semideserts wherever sodium is available either as chloride or sulphate or as products of efflorescence of sodium silicates. The carbonate ion is derived from calcium carbonate and bicarbonate or from carbon dioxide in air, the formation of sodium carbonate being catalyzed by thinly dispersed aluminium silicates and in part promoted by the action of micro-organisms.[3] Mountainous alkaline lakes of volcanic origin contain soda originating from their springs and accumulating over many years: investigations seem to point to sodium bicarbonate as the parent substance. In some lakes in the Western Hemisphere the lake water may be strongly alkaline while the springs are acid.[4] There appears to be no evidence for the formation of alkali carbonates in the soil by direct reaction of chlorides or sulphates with calcium carbonate. Sulphates, being more soluble than chlorides, accumulate in the underground waters and under the action of saline vegetation and algae are said to be reduced to sulphides and transformed to carbonates by the carbon dioxide in the air.[30] The irrigation of saline soils needs care and forethought since it may produce results quite opposite to those desired. The level of the salty subterranean water may be raised, the waters may concentrate in the more superficial strata, and alkali may appear, rendering the soil even less adapted to plant life; the presence of neutral salts such as sodium chloride and sulphate is an obstacle to the formation of soda, and their exhaustion is a necessary preliminary for the conversion of a saline to an alkaline soil. Sodium adsorption compounds appear to be formed with certain zeolites and colloidal organic acids, which enter into reactions only in the absence of the salts from which they are derived. On dispersion these coagulated colloids are hydrolyzed; the resulting sodium hydroxide can then react with calcium carbonate or pass to soda by absorption of carbon dioxide.[5,6] An Indiana soil initially of pH 5·0 showed, after treatment with sodium chloride, a progressive rise to pH 7·8 on leaching. The products of hydrolysis together with the hydroxyl ion promote deflocculation.[7] The well known black alkali lands contain soda and no free carbon dioxide; the soda content may be reduced to an equilibrium concentration of 25 p.p.m. in the soil solution by addition of gypsum, while the application of organic matter and good cultivation may enable aerobic soil bacteria to produce carbon dioxide and so transform the residual soda into innocuous bicarbonate.[8] Free sulphur undergoes active oxidation in such soils to give products which eventually remove all soluble carbonate.[9] In addition to the above exchange decompositions, soda may be formed by the hydrolysis of sodium silicates or by their exchange with calcium and magnesium bicarbonates in the ground waters; it is said that the biochemical reduction of sodium sulphate with the formation of hydrogen sulphide takes place only in petroleum waters.[10]

LOCATION OF THE MORE IMPORTANT SODA LAKES AND DEPOSITS

The methods adopted for the commercial exploitation of soda deposits are discussed later.

Africa

Egypt.

The topography and geochemistry of the soda lakes are much akin to those of East Siberia, Africa and U.S.A.[3]

Kenya.

Almost inexhaustible supplies of soda are to be found in the volcanic range.[11,12] In addition there are the enormous deposits (estimated at 20m tons of sesquicarbonate) and the waters of Lake Magadi[13,14] where the lake crust is of fairly uniform composition giving Na_2CO_3 42·67–49·40, $NaHCO_3$ 29·03–38·20, NaCl 0·80–3·86, H_2O 15·99–18·35 and insoluble matter 0·19–7·65%; the mother liquor in the crust is almost as rich in sodium chloride as in carbonates. The deposit is attributed to a decomposition of nepheline ($(Na,K)AlSiO_4$), by hot springs and by carbon dioxide which comes up through cracks in the vicinity.[15] The analysis above corresponds to nearly pure sesquicarbonate (trona), $Na_2CO_3,NaHCO_3,2H_2O$, but further south in the Little Magadi and Lake Natron the carbon dioxide is so abundant that the trona is changed to bicarbonate, which is somewhat uncommon in nature. Some layers are red; the colour has been variously attributed to the dye from flamingo feathers[16] and to the presence of microscopic organisms.[17]

Libya.

Workable quantities of alkali are found at Fezzari.

South Africa.

The Pretoria and Matzap salt pans average approximately $NaHCO_3$ 0·8, Na_2CO_3 8·2, NaCl 15·5 and H_2O 75·5%. The process of extraction involves concentration to at least 17·7% Na_2CO_3.[18]

Tanganyika.

Deposits occur at Moshi.[1]

America

Argentine.

A large deposit exists at El Rincón (Andes) containing Na_2CO_3 56·27, Na_2SO_4 20·16, NaCl 12·32, $NaHCO_3$ 8·27, SiO_2 2·16, H_2O 1·00 and insoluble matter 0·70%. The possible annual yield is estimated as 5000 tons of Na_2CO_3.[19]

Brazil.

Salt lakes are very common in the interior. Soda lakes have been discovered in 32 localities analyzing Na_2CO_3 23–41, NaCl 1·5–10, Na_2SO_4 1–7, $MgSO_4$ 0·4–2·2, insoluble matter 11–16, and H_2O 40–52%. There are also three nitrate lakes and one large sodium sulphate lake.[20]

Canada.

The located areas are mostly in British Columbia; there are sodium carbonate deposits near Prince George,[21] while the lakes of the Green Timber Plateau have soda and other soluble salts in the brines and in cold weather 'winter' crystals of soda form with less than 2% of impurities; it also occurs as an impure crystalline deposit contaminated with mud. Under present conditions solar evaporation exceeds dilution of the brine by springs and surface drainage in many lakes.[22] Soap Lake in the Ashcroft map-area of British Columbia lies about 7 miles by pack trail to the south of Spence's Bridge on the C.P.R. The lake is about 1 mile long and at most 450 yards wide but varies in size with the dryness of the season. When the water level is low the shore is covered with white salts about an inch in depth. The brine analyses (in p.p.m.): K zero, Na 60018, Mg 169, Cl 2439, SO_4 5900, HCO_3 10697, CO_2 67700, total 146923. Profitable recovery depends upon overcoming the difficulties of transport.[23] There are large reserves of sodium and magnesium salts in Manitoba and Saskatchewan.[24] Many million tons of Glauber's salts are said to be available in Canada. It has been suggested that the reaction $Na_2SO_4 + BaCO_3 \rightarrow Na_2CO_3 + BaSO_4$ should be applied to the manufacture of sodium carbonate; the equilibrium point is at 50% conversion, but it is reported that with a 'catalyst' (undisclosed) a 90% yield can be obtained.[25]

Chile.

There are workable deposits at Antafagasta.[1]

Mexico.

The natural saline waters have been made the subject of patents for the extraction of bicarbonate by solar concentration and treatment with carbon dioxide, alone or with ammonia.[26] The brines are contained in the bentonite clays of Lake Tezcuco. Tequezquite (sometimes called confitillo or tepalcate or espumilla) is the name given to the alkaline earths collected from the Mexican lakes and lagoons. "Several attempts to establish an industry have been abandoned". The average composition of the deposits is Na_2CO_3 20–5, NaCl 25–30, KCl and K_2CO_3 5–10, combined water and moisture 10–5, insoluble material 30–40%. The northern part of the lake contains more potassium salts and sodium chloride than the southern. Iodine is occasionally reported. The preferred method of separation from the sand and colloidal clays is to mix the earth with ice or snow, lowering the temperature to −18 or −20°C., when the sodium carbonate is almost insoluble in the saturated sodium chloride. It is said that the lake deposits could supply the requirements of Mexico in sodium salts for 200 years.[28] There are also small deposits in the state of Sonora in North-western Mexico.[27]

Peru.

Extensive study of the saline waters near the coast at Chilca shows the possibility of their economic exploitation.[29] In southern Peru near the village of Ica the deposits average 20% bicarbonate and carbonate of soda in varying proportions with 35% of sodium sulphate, some sodium chloride and water. A study of similar deposits near Pisco indicates that the sulphate— more soluble than the chloride— accumulates in the underground waters near the surface (at a depth of 1 to 3 m.), and under the action of saline vegetation and algae are slowly reduced to sulphides which are then transformed to carbonates by the carbon dioxide of the air.[30]

United States.

In a total production of 5,327,199 tons in 1957, there were 676,611 tons of natural soda.[31] There are waters of high sodium bicarbonate content in the Atlantic and Gulf coastal plains. There seems to be no possibility of there being enough carbon dioxide produced by oxidation of organic matter to account for this. If the waters are shaken with lignitic material (serving as a source of carbon dioxide), calcium carbonate and a base-exchange material, a considerable increase in sodium bicarbonate content is observed. If the base-exchange material is absent, a water rich in calcium bicarbonate results.[32]

California.

In mineral production in 1949 petroleum and natural gas, cement, sand and gravel, gold, stone products, boron minerals, soda and salt ranked in that order.[33] Owens Lake is a closed basin in the deserts of the southern part of Inyo County, California, and is a source of soda, sesquicarbonate and borax.[34] A representative analysis of Owens Lake brine gave Na_2CO_3 9, $NaHCO_3$ 1·2, $Na_2B_4O_7$ 1·0, Na_2SO_4 3, NaCl 16, KCl 1·5, H_2O 74·47%. The diversion of the Owens River in 1917 resulted in the drying up of the Lake, which is however occasionally flooded.[36] In Searles Lake (San Bernardino County) *nahcolite,*[35] sodium bicarbonate, occurs in rich beds below the central salt-crust at various depths from 122 ft. to the bottom of the drilling at 289 ft. In the upper levels it occurs in a thin bed in association with *gaylussite, trona, thenardite* (Na_2SO_4) and *northupite;* in intermediate levels with *gaylussite, burkeite* and *thenardite;* below 170 ft. (the principal deposits) it is in *gaylussite* or *northupite* marls free of other saline minerals. It is suggested that it may have originated by reaction of trona and calcium bicarbonate with the production also of either calcite or gaylussite, perhaps at temperatures slightly lower than those now existing in the deeper brines (22·5°C.); below 21·26°C. *nahcolite* and soda are the stable phases.[38] The Searles Lake brine has pH 9·48 corresponding to Na_2CO_3 78 and $NaHCO_3$ 22%, or to $Na_2B_2O_4$ 71 and $Na_2B_4O_7$ 29%; by making up artificial brines from solutions of sodium and potassium chlorides and sodium sulphate and adding buffer salts the 'salt effect' can be made constant[39] and equal to that in lake brine, which averages Na_2CO_3 4·7, $Na_2B_4O_7$ 1·5, Na_2SO_4 7·0, NaCl 16·4, KCl 4·8, H_2O 65·4%.[36,37]

Borax Lake in Lake County contains some carbonate. The desert town of Trona produces only potassium salts.

Idaho.

Equilibrium studies of sodium carbonate and bicarbonate in Idaho soils extended over a period of 2 years, one series being kept at optimum water content, the other air dry. On addition of either sodium carbonate or sodium bicarbonate an equilibrium content is reached; the sodium carbonate series showed bicarbonate in the aqueous extract immediately after mixing, and conversely with sodium bicarbonate additions.[40]

Nebraska.

Alkali brines in Western Nebraska are exploited commercially.[41]

Nevada: Ragtown Soda Lakes (near Carson Sink).

The deposits average: Na_2CO_3 45·1, $NaHCO_3$ 34·66, Na_2SO_4 1·3, NaCl 1·6, insoluble material 0·8, H_2O 16·2%.[1]

Oregon.

Summer and Abert Lakes in Lake County contain chiefly soda with appreciable sodium chloride and sulphate; in Alkali Lake the composition of the salts from different potholes varies considerably, but several are high in soda (up to 53%) with relatively low content of other salts (down to 4·4%); this lake may contain 75,000 to 200,000 tons of sodium salts.[42]

Washington.

Wilson Creek, some 100 miles west of Spokane, has a lake with a deposit consisting largely of mixed hydrates of sodium carbonate and has been worked commercially.[1]

Wyoming.

In Sweetwater County, trona has been found in thicknesses up to 10 ft. at depths of 1500 ft. during boring for oil.[43] Important brines occur in the Union Pacific Lakes near Green River.[44]

Venezuela.

There are alkali deposits in Lagunilla Valley.[1]

Asia

China.

Extensive deposits of natural soda are located in the 'nor' lakes of North Manchuria and Mongolia;[45] these in 1929 were still worked by primitive methods.[46] The United Nations Statistical Digest estimates that the total Chinese production of soda in 1955 was about 1·7 thousand metric tons. It would be reasonable to assume that big efforts are being made to work natural sources and to establish factories. A large deposit of gaylussite occurs in the Dtabusu-nor Lake in Kirin, Inner Mongolia. During the dry season the lake is covered with an efflorescent incrustation containing soda and thermonatrite with halite and thenardite.[47] There are strongly alkaline top soils (pH = 10·1) occurring in the flooded areas along the Yellow River and where water seeps up from the subsoil containing 8·5% of total solids (carbonates, chlorides and sulphates) and 0·8% of carbonate.[48] There are many other known localities including Sin-Yuan, Heilungkiang, Kirin, Liao-Ning, Jehol, Chahar, Shansi, Shensi, Kansu and the alkali deserts of Tibet.[1]

India and Pakistan.

Efflorescent soils occur in many places. The surface incrustations in which sodium carbonate and sulphate occur are known as reh or synonymously kalar, thur, or sajji-matti. The principal factors in the formation of reh soils appear to be (1) alternating intensely dry and wet seasons, (2) low gradients with slopes less than 5 ft./mile, (3) a high water table, (4) rocks rich in soda minerals, (5) the nature of the ground and canal water, and (6) base-exchange reactions.[49] The reh incrustation contains (averaged from 500 analyses); insoluble matter 3·3–8·4, Na_2CO_3 48·2–60·2, NaCl 0·2–4·3, Na_2SO_4 0·3–7·2, H_2O 30·3–38·2% and a little organic matter. The soda can be purified to yield a product of about 90–95% Na_2CO_3 which can be used in the manufacture of coloured glass,[52] crude caustic and soap as at Parantiz, Ahmedabad District.[53] It has been estimated that the reh soils in the United Provinces would yield by scraping some 5,000,000 tons of soda annually.[54] The reh soils occur in areas where there is no vegetation, known as Usar lands. The soil analyses (28 samples) show wide variation, but average:- SiO_2 69·3–85·4, Fe_2O_3 0·9–8·2, CaO 0·8–9·8, MgO 0·4–2·4, Na_2CO_3 1·6–23·5, NaCl trace to 16·5, and Na_2SO_4.[51]

There are 'earth-soda' deposits at Dodmole near Chamarajanagar, District of Mysore, containing soda, bicarbonate, sodium sulphate, chloride, and ferric oxide. 5,000 sq.yds. give ten tons of earth soda from which by washing 200 lb. of soda are recovered, a 9% yield.[50]

Dry lakes yield a crust containing kharo, which is a mixture of decahydrate, monohydrate, and sesquicarbonate with a soda brine (Na_2CO_3, NaCl, Na_2SO_4, $NaHCO_3$).[55] It is also deposited on the bottom of the shallow alkaline lakes near Khaipur, Sind during the summer.[56,57]

U.S.S.R. (Asia and Europe).

There is a wide distribution of salt lakes and deposits over this enormous area. Prospecting for new soda deposits should be done where there are well lixiviated soils, sands, and old river channels, and in regions of everlasting cold.[10] All sediments from the soda lakes of west Siberia contain ferrous sulphide formed by the biochemical reduction of sulphates to hydrogen sulphide, and organisms of the type *Microspira aestuarii* var. Tambi are found. Ferrous sulphide may be converted to sodium sulphide which would yield soda by the action of carbon dioxide.[59,60] The Kulunda valley in the Slavgorod district contains eleven systems of chains of lakes and swamps joined by streams and springs. The first lake of a chain contains specifically water in which $CO_3^{2-} + HCO_3^- > Ca^{2+} + Mg^{2+}$; lakes extending to the edge of the surrounding pine woods are characterized by $CO_3^{2-} + HCO_3^- < Ca^{2+} + Mg^{2+} < CO_3^{2-} + HCO_3^- + SO_4^{2-}$, derived from the weathering of the annual flora growing in the black soil of the steppe; they contain largely magnesium sulphate and no sodium carbonate. Two other types are recognized farther down the chain: $CO_3^{2-} + HCO_3^- + SO_4^{2-} < Ca^{2+} + Mg^{2+}$ and finally $HCO_3^- = 0$.[62] The soda lake Laka Tanata,[63] is in the Kulundina desert. The surface waters in these depressions are all of the $Na-CO_3$ type. It seems that the climatological conditions of the more arid period of interglacial time were favourable to the production of Cl^-, SO_4^{2-}, Na^+, and Mg^{2+}, which are enriched in the end states of the salt-lake deposits, while the higher humidity and cooler conditions of the post glacial recent period favour soda leaching from desert bottoms.[61] The Mikhailov Lakes in the Altai region of the Don valley, the soda lake Abalakh in Yakutim (Siberia),[65] and the Doroninsky soda lake, which has a total reserve of salts of some 1,000,000 tons,[64] have brines containing Na_2CO_3 5–11, $NaHCO_3$ 1–2, NaCl 3–7 and Na_2SO_4 1–3%. On cooling sodium carbonate decahydrate crystallizes, containing mirabilite ($Na_2SO_4,10H_2O$) in solid solution.[66–68] In the larger deposits there may be as much as 90–98% of sodium carbonate decahydrate. This may form a cement-like solid with the sands and silts. In the Barabinsk lowlands the solonchak series of soils has been classified; there is an accumulation of carbonate and bicarbonate of soda with a specific quantitative variation. Aqueous extracts have generally a high soda content (100 milliequiv./l. of $NaHCO_3$ and 2–10 milliequiv./l. of Na_2CO_3). Six geochemical landscape units are recognized, each with its specific chemical characteristics arising from the complex reactions occurring between the ground water, the soil and decayed vegetation. They extend between the limits of the bicarbonate of the alkaline earths through sulphate and chloride enriched with sodium carbonate to sulphate and chloride of sodium with some magnesium. Extensive chemical analyses of these units are available.[69,70] The Petukhov lakes about 210 km. from Slavgorod in Siberia are saturated with sodium carbonate. When the temperature drops below 0°C. the smaller lakes precipitate the decahydrate in layers 8–15 cm. deep. This is mined and dehydrated by exposure to the sun. The total amount of salt calculated as anhydrous soda dissolved in the lakes is 2·6 million tons with about twice this amount deposited at the bottom of the lakes. The self-precipitated soda analyses Na_2CO_3 36·46, NaCl 0·39, Na_2SO_4 trace, H_2O 62·16%. The soda is said to be 'incomparably superior' to the products mined in California, Egypt or East Siberia.[71]

A partial examination of the ternary system $NaHCO_3-Na_2SO_4-H_2O$, particularly in the relation of the equilibria to conditions in Siberian salt-lake brine, has been carried out by measuring the simultaneous solubilities of sodium bicarbonate and sulphate in the presence of carbon dioxide at 0°, 20°, 25°, 30° and 45°C.[72] The Caspian Sea region has a number of salt lakes and deposits.[1] Other deposits occur in the Lake Baikal region, Slavgorod, at Berezniki[73] and in Armenia at the Araxes Plain lakes. In Turkistan soda is obtained from green branches of saksaul (*Haloxylon ammodendron*) which are burned in open pits and the ashes ground and leached at 70–80°C. The solution of specific gravity 1·08 is concentrated to 1·32 and the salt (Na_2CO_3 20·7, K_2CO_3 2·03%) is crystallized out.[74]

Europe

Germany.

Sodium bicarbonate and iodide occur in certain waters of East Prussia.[75] In the deeper underground waters of the Mayence Basin sodium bicarbonate occurs, but calcium and magnesium are nearly always missing. The HCO_3^- content varies between 5·8 and 12·5 milliequiv./l.: only the springs of Weilbach and Offenbach show a higher value (16·3–32 milliequiv./l.); in the waters from the Tertiary and Diluvium, however, HCO_3^- and SO_4^{2-} are mostly bound with Ca^{2+} and Mg^{2+}. In the sodium chloride springs on the southern border of the Taunus the content of earth alkali, with calcium preponderant, varies between 10 and 30 milliequiv./l.[76]

Italy.

Saline incrustations collected west of Naples in the latter part of the 19th century were given the name *thermokalite*; on re-examination they were shown to consist of a mixture of trona, thermonatrite, thenardite, free sodium bicarbonate, and no potassium salts. The bicarbonate constitutes over 20% of the mass and the name *nahcolite* (NaHCO-lite) was suggested for it.[35]

Hungary.

There are soda deposits in the Szegedin district.[1]

EXTRACTION

Much research has been done on the chemistry of the commercial exploitation of brines and deposits; based generally on the specific application of the phase rule to the systems involved. The work is often the subject of patents and only meagre details are available, within the widest limits, of temperature, concentration and materials. The following examples out of very many are illustrative of the extraction of soda from brines, mostly of the Owens and Searles Lakes types; they are applicable to solutions containing minimal sodium sulphate. A survey of plants producing natural soda ash in the Owens and Searles Lakes district was carried out in 1921,[77] but presumably is much outdated. At about the same time a general account of the treatment of saline water at Owens Lake indicates that: (1) insoluble matter and calcium and magnesium carbonates are precipitated in pools; (2) trona is crystallized out in other pools after evaporation by solar heat; (3) the liquid is drawn off before salts deposit; (4) in cold weather it is largely sal soda that separates; leading carbon dioxide into the pools aids the formation of the desired bicarbonate.[78,79] It will be seen from the examples cited below that the majority of patented processes do in effect involve modifications of this treatment.

(i) The decahydrate is obtained by stirring a complex or natural brine with excess of solid sodium chloride and mono- or decahydrate, above 20°C., until equilibrium is obtained. After the excess salts (sodium carbonate and sulphate) have settled, the brine is chilled to just above 0°C. to allow the major part of the sodium carbonate to crystallize as decahydrate, which is washed and calcined for soda ash.[80-84,41]

One patent was granted for chilling the brine to a temperature somewhat above 0°C. to cause precipitation of $Na_2CO_3;10H_2O$ and the crystals are separated from the brine'. The brines may be evaporated until the precipitating salts show just under 0·6% of chloride; they are separated, redissolved in water, and recrystallized for sodium carbonate. The carbonates and chlorides may be separated by hydraulic classification.[85] Much use is made of solar heat; natural brines containing soda and potassium chloride are subjected to solar evaporation until the residual deposit is a slush; this is leached with boiling water, and the leach liquor evaporated by solar heat and artificial heat to give potassium chloride on cooling. The slush residue is mixed with an aqueous solution containing carbonated slush (sodium bicarbonate) amounting to one-third of the weight of slush treated; the liquor is agitated at 40°C. and the product (probably trona) is filtered off, washed, dried, and calcined.[86]

(ii) If dissolved silica is present it may be prevented from separating by treating with adequate caustic alkali and chilling to precipitate the decahydrate.[83] If the silica content is less than 1% it is removed by treatment with sodium aluminate to give, on standing, a precipitate largely of alumina and silica.[87]

Organic matter and iron are removed from Wyoming trona dissolved in hot brine (80–100°C.) by adding activated charcoal to approximately 0·125% by weight of the brine.[90]

(iii) The pure heptahydrate may be had by suspending crude solid decahydrate in a brine saturated with sodium chloride and containing less than 5% of sodium sulphate at 28–31°C., cooling to not lower than 10°C. and separating the crystalline heptahydrate.[88,89] The mother liquor may be used again and again until the sodium sulphate content reaches 6%: it is then discarded; or burkeite may be isolated.[91]

(iv) The monohydrate can be separated by agitating brine with mixtures of solid sodium chloride and any modification of sodium carbonate except the monohydrate, warming to 30°C. (at which temperature the brine is highly supersaturated with respect to the monohydrate), removing undissolved matter, and raising the temperature to above 31°C. The monohydrate begins to separate; the temperature is lowered to just above 24°C. until equilibrium is attained, when the monohydrate is removed and washed free from mother liquor.[92] Alternatively the brine may be concentrated at approximately the boiling point of water to separate some of the carbonate as monohydrate.[44,93-95]

(v) (Carbonation processes). The Owens Lake or other complex brine containing soda and borax is treated at 35–45°C. with a gas containing carbon dioxide (e.g., flue gases in the initial stages) to cause precipitation of sodium bicarbonate; this also decreases the solubility of borax in the brine. The carbonation is discontinued while there is still some sodium carbonate in the brine.[96-99] The brine may be chilled to a temperature of about −14°C. to effect precipitation of carbonate, sulphate and borax; the precipitated salts are warmed to melt the sodium carbonate decahydrate (the unmelted salts being separated) and the cleared liquor carbonated to precipitate sodium bicarbonate.[100-102] Carbon dioxide and ammonia may be fed into the brine to simulate conditions in the Solvay process, with the precipitation of sodium bicarbonate.[103] Crude trona can be treated to recover bicarbonate, which will be subsequently calcined to give soda ash by dissolving it in an unsaturated solution of bicarbonate and carbonate, in effect the mother liquor. The proportion of bicarbonate to carbonate in the mother liquor is 9·5:20 at 60°C. and 18:16 at 100°C. Carbon dioxide is added to the system in the amount necessary to convert the carbonate of the trona to sodium bicarbonate. The solution is cooled to crystallize the bicarbonate, which is separated, and the mother liquor is recycled.[104] During the process, hydrogen sulphide may be eliminated from the raw Searles Lake brine by reducing the pH from 10 to 9 and gassing with an air-carbon dioxide mixture; hydrogen sulphide is liberated and bicarbonate precipitated.[105]

(vi) The sesquicarbonate can be produced in a three-stage continuous cyclic process from fresh soda brine, which is treated with bicarbonate to precipitate the sesquicarbonate until the alkalinity is sufficiently reduced to stop the precipitation; the product is filtered off, and carbon dioxide is added to the mother liquor to precipitate the bicarbonate, which is withdrawn and used again. The sesquicarbonate is slightly contaminated with bicarbonate and borax.[106]

Trona itself may be calcined to drive off carbon dioxide and water and then be redissolved, the solution being added to the suspending brine described in (iii).[89] It may also be recrystallized from a brine of soda and bicarbonate.[107]

(vii) The use of ion-exchange resins has been applied largely to sea water. Organic cation-exchange materials such as sodium exchange resins react with magnesium bicarbonate to exchange Na^+ and Mg^{2+}, forming sodium bicarbonate and a Mg^{2+}-resin from which the Na^+-resin is regenerated by treatment with sea water.[108-111]

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THE INDUSTRIAL PRODUCTION OF SODIUM CARBONATE

The Solvay or Ammonia–Soda Process

Mellor II, pp. 737–747, gives an adequate account of the outlines of this process with references dating up to 1910. The fundamental principles of operation have hardly changed since then, but much has been done by strict physico-chemical control at all stages to reduce the chances of economic failure. The published work largely appears in patent specifications, but there has been much research into the equilibria involved particularly in Japan and Russia. The industry appears to have a long tradition of commercial secrecy, quite understandably as to methods but less so as to quantity and utilization statistics. In compiling the following supplement constant reference has been made to the excellent and detailed account in Thorpe's Dictionary of Applied Chemistry,[1] and to T. P. Hou's book 'Manufacture of Soda'.[2]

To provide a framework it will be necessary to emphasize once more the steps in the process, which is essentially the conversion of limestone and salt into sodium carbonate and calcium chloride. The equilibrium in the reaction $CaCO_3 + 2NaCl \rightleftharpoons CaCl_2 + Na_2CO_3$ lies almost wholly towards the left and cannot be practically reversed except in stages and by the addition of energy. The following reactions are those by which the desired end is usually achieved. Losses in the recycled material inevitably occur and much of the success of any soda-ash factory will depend on reducing these to a minimum.

The flow diagram for the process is given in Fig. 1.[1]

The following compilation of thermochemical data associated with the process may be found useful. It has been put together from normally available sources[2] or from papers to which reference has been made in the course of this revision.

Heats of formation (g.-cal. per g.-mol.): ammonium bicarbonate, NH_4HCO_3 (aq.) 199,000, (anhydrous) 208,600; ammonium carbonate, $(NH_4)_2CO_3$ (aq.) 221,600; ammonium chloride, NH_4Cl (aq.) 72,800; ammonia, NH_3 (g.) 12,000; carbon dioxide, CO_2 (g.) 94,500; sodium bicarbonate, $NaHCO_3$ (anhydrous) 227,700, (aq.) 222,700; sodium chloride, NaCl (aq.) 96,600 and water, H_2O (l.) 69,000.

Heats of reaction (g.-cal. per g.-mol.):

$$2NH_3\ (\text{aq.}) + CO_2\ (\text{aq.}) + [H_2O] \rightarrow (NH_4)_2CO_3\ (\text{aq.});\quad \Delta H = -16{,}850$$

$$CO_2\ (\text{g.}) + \text{aq.} \rightarrow CO_2\ (\text{aq.});\quad \Delta H = -5{,}880$$

$$NH_3\ (\text{g.}) + \text{aq.} \rightarrow NH_3\ (\text{aq.});\quad \Delta H = -8{,}430$$

$$(NH_4)_2CO_3\ (\text{aq.}) + H_2CO_3\ (\text{aq.}) \rightarrow 2NH_4HCO_3\ (\text{aq.});\quad \Delta H = -8{,}400$$

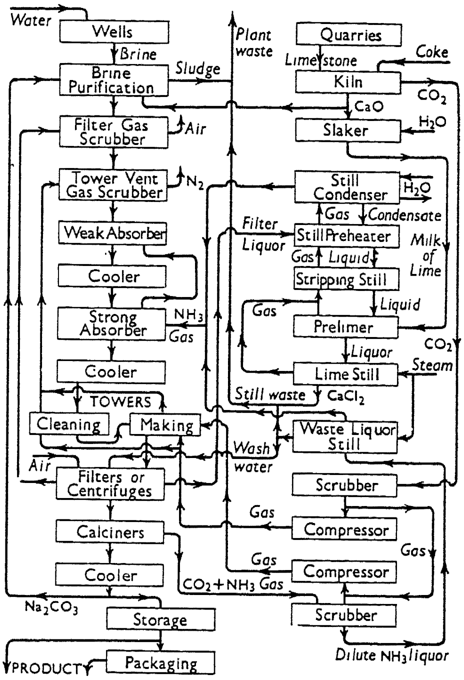
Water
Wells
Brine
Brine Purification
Sludge
Filter Gas Scrubber
Air
Tower Vent Gas Scrubber
N_2
Weak Absorber
Cooler
Strong Absorber
NH_3
Gas
Cooler
TOWERS
Cleaning
Making
Air
Filters or Centrifuges
Calciners
Cooler
Na_2CO_3
Storage
PRODUCT
Packaging
Plant waste
Quarries
Limestone
Coke
Kiln
CO_2
CaO
Slaker
H_2O
Still Condenser
H_2O
Gas
Condensate
Filter Liquor
Still Preheater
Milk of Lime
Gas
Liquid
Stripping Still
Gas
Liquid
Prelimer
Liquor
CO_2
Steam
Lime Still
Still waste
$CaCl_2$
Waste Liquor Still
Wash water
Scrubber
Gas
Compressor
Gas
Gas
Compressor
CO_2+NH_3 Gas
Scrubber
Dilute NH_3 liquor

FIG. 1. FLOW DIAGRAM OF AMMONIA-SODA PROCESS

$$NH_4HCO_3\ (aq.) + NaCl\ (aq.) \rightarrow NH_4Cl\ (aq.) + NaHCO_3\ (aq.);\ \Delta H = +100$$
$$NH_4HCO_3\ (aq.) + NaCl\ (aq.) \rightarrow NH_4Cl\ (aq.) + NaHCO_3\ (s.);\ \Delta H = -4,900.$$

Finally:

$$NaCl\ (aq.) + NH_3\ (g.) + H_2O\ (l.) + CO_2\ (g.) \rightarrow NaHCO_3\ (s.) + NH_4Cl\ (aq.);\ \Delta H = -28,400.$$

This corresponds to a total heat effect of 536,000kg.-cal. per ton of soda ash. In the processing there must be added at 75% ammonia efficiency some 860,000 kg.-cal. per ton for the condensation of steam carried to the absorber by the ammonia gases. The making towers therefore need intensive cooling to remove this together with approximately 89,000kg.-cal. due to the lowering in temperature of the precarbonated liquor from 38·5°C. to the draw at 22°C.

Step 1. Carbon Dioxide Supply. $CaCO_3 \rightarrow CaO + CO_2$.

In most countries carbon dioxide is obtained by heating limestone. In the United States on the Gulf Coast, material from large deposits of oyster shells has been calcined, yielding a high quality lime; the existence of these deposits, the presence of salt domes, the occurrence of natural oil and gas, the co-operative use with oil processing plants and others of centralized steam supplies and electric power all make for economy and simplicity in operation, and have accounted for the shift of the soda-ash and allied industries into Louisiana and to the Gulf Coast.[2]

The actual total lime consumption for 100kg. of 98·8% Na_2CO_3 is said to be 58·35kg., the calculated quantity being 52·2kg. These and related figures are considered at some length in papers on the management of the lime kiln in an ammonia-soda plant.[3,4]

The use of enriched water gas has been proposed in which hydrogen is a diluent instead of atmospheric nitrogen; the unabsorbed gas is substantially pure hydrogen and may be used in ammonia synthesis.[5] Brown coal can be advantageously used in this manner.[6]

Step 2. Ammoniation of the Brine.

The typical plant brine contains about 3·06 g. of sodium chloride per l., *i.e.* h = g.-mol. of water per g.-mol. of NaCl + NH_4OH = 9·5. The gas from the still (Step 4) contains with each g.-mol. of ammonia 0·20 g.-mol. of carbon dioxide and 0·40 g.-mol. of water. The absorption is allowed to proceed until the cation index $[NH_4^{\cdot}]/([Na^{\cdot}]+[NH_4^{\cdot}])$ is 0·50; lower values produce poor sodium bicarbonate yields; higher values may precipitate sesquicarbonate in the liquor and ammonium bicarbonate in the carbonating towers. Heat is liberated during the absorption and the liquor is cooled, the temperature on leaving the final coolers being about 35°C. The brine may undergo a preliminary 'external' lime-soda purification by agitation with a slight excess of soda ash to remove Ca^{2+}, and calcium hydroxide suspension to remove Mg^{2+}.[7] 'Internal purification' consists in ammoniating the brine with sufficient ammonia + carbon dioxide to precipitate calcium carbonate and Na_2CO_3, NaCl,$MgCO_3$ (northupite). The addition of northupite crystals before cooling the brines precipitates 90% of the magnesium and prevents later trouble caused by slow precipitation of northupite.[8] The physical and chemical conditions necessary for maximal removal of other foreign ions such as calcium, magnesium, iron and aluminium from natural brines have been considered from the points of view of temperature, stirring rates and concentrations.[10] Inability to effect this purification with a magnesium-rich brine, coupled with loss of ammonia and too high summer temperatures, were responsible for the initial failure of the Solvay process in Japan.[9]

Tables of the solubility of sodium chloride in aqueous ammonia are available.[2] The solubilities of the various substances present during the process are of course influenced by common-ion and salting-out effects, and often depart largely from the values for the pure substance in water.

Step 3. Carbonation.

The carbon dioxide passes to the carbonating towers or columns where it is absorbed by the ammoniacal sodium chloride brine. The reaction $NaCl + NH_4OH + CO_2 \rightleftharpoons NaHCO_3 + NH_4Cl$ is reversible, and although the fundamental step in the process is the precipitation of sodium bicarbonate, it has nevertheless an appreciable co-solubility with ammonium chloride so that about 70–75% of sodium ion is precipitated as bicarbonate.

For optimum working the carbon dioxide concentration cannot be arbitrarily set. The conditions in individual columns must be considered, but the highest possible concentration is desirable and 60–85% of carbon dioxide in the gas can be used if the column is suitably adapted; the level of the liquid in the column may then be lowered.[11] However, increase in carbon dioxide pressure above 1 atm. has little effect.[12] It is important to maintain low temperatures in the upper parts of the columns.[13] The precipitation is accompanied by the emission of some 370,000 kg.-cal. per metric ton of the bicarbonate.

The equation given above does not represent anything but the reactants and resultants. Ammonium bicarbamate is initially formed. The basic stages of the carbonation process are said to be:

(i) The hydration of carbon dioxide mainly by (a) $CO_2 + OH^- \rightarrow HCO_3^-$ and (b) $CO_2 + H_2O \rightarrow H_2CO_3$, the first being predominant in the initial stages.

(ii) The formation of carbamate by $CO_2 + 2NH_3 \rightarrow NH_4^+ + NH_2COO^-$, this reaction being always much faster than (i,b); also since $[NH_3]$ is always several thousand times higher than $[OH^-]$, by far the greater part of the absorbed carbon dioxide is used in making carbamate. It is probable that two successive bimolecular steps are involved in this: (a) $CO_2 + NH_3 \rightarrow H^+ + NH_2COO^-$ and (b) $NH_3 + H^+ \rightarrow NH_4^+$.

(iii) The hydrolysis of the carbamate, $NH_2COO^- + H_2O \rightarrow HCO_3^- + NH_3$, probably involving (a) $NH_2COO^- + NH_4^+ \rightarrow 2NH_3 + CO_2$ and (b) $CO_2 + OH^- \rightarrow HCO_3^-$, the latter step being slow and velocity-limiting.

NH_3 is converted to NH_4^+ only at low pH; in alkaline medium (pH $\nless$ 8) free ammonia accumulates in the solution as a result of (iii). The reaction is stimulated by the precipitation of bicarbonate, resulting in the removal of HCO_3^- from solution while (ii) consumes the accumulated ammonia.[14,15]

The theory of gas absorption accompanied by chemical reaction in the liquid phase has been extensively examined in a series of Russian investigations applied to the field of the ammonia-soda process. The absorption of carbon dioxide appears to be mainly determined by diffusion within the liquid film, since the rate equation N = rate of absorption in g./sq.cm./sec. = $K_l (P_g - P_l)$ holds: here K_l = liquid-film coefficient, P_g = partial pressure of carbon dioxide in the bulk of the gas, and P_l = its equilibrium pressure over the liquid. It is interesting to find that N may fall to zero at high bicarbonation indices even when $\Delta P = P_g - P_l$ is as high as 100–170 mm. of mercury. This cessation of absorption when the driving force ΔP is still high may perhaps be explained by the slowness of the processes of hydration of carbon dioxide and crystallization of bicarbonate resulting in the accumulation of free ammonia as in (iii) above.[14,16,17]

Systematic measurements of the velocity of absorption of carbon dioxide have been made. The absorption rate for varying sodium carbonate content at 15°C. is given in Table I.

TABLE I.- RATE OF ABSORPTION OF CARBON DIOXIDE IN SODIUM CARBONATE SOLUTION

Na_2CO_3, g./100 g. H_2O	CO_2 absorbed, cu.mm./sec./sq.cm.
6	1·875
8	1·829
10	1·666
12	1·470
15	1·250
18	1·064
20	0·986

The effect of the addition of sodium bicarbonate to a solution containing 6 g. Na_2CO_3 per 100 g. of water is shown in Table II.

TABLE II.- EFFECT OF $NaHCO_3$ CONTENT ON RATE OF ABSORPTION OF CARBON DIOXIDE

$NaHCO_3$, g./100 g. H_2O	Absorption rate (cu.mm./sec./sq.cm.)
0	1·875
2	1·500
4	1·180
6	1·000
8	0·891

Similar data for sodium chloride are given in Table III.

The effect of temperature changes was also studied. If the liquid is not stirred the rate of absorption drops by half.[18,19]

At this point it may be pertinent to mention important work on the principles involved in physical degassing. A summary of these discusses the influence of surface tension and the significance of gaseous diffusion. Exchange coefficients have been calculated for the surface of the solution, for the gas

Refs. p. 1082

TABLE III.- EFFECT OF SODIUM CHLORIDE CONTENT ON RATE OF ABSORPTION OF CARBON DIOXIDE

NaCl, g./100 g. H_2O	Absorption rate (cu.mm./sec./sq.cm.)
0	1·875
4	1·864
8	1·666
12	1·250

bubbles in the bulk, and for the passage of dissolved gases from water drops into the surrounding atmosphere. Values were obtained for carbon dioxide, oxygen and ammonia. The rate of decomposition of sodium bicarbonate during thermal degassing was determined experimentally and checked operationally.[20] The partial pressures of ammonia and carbon dioxide over the carbonated ammoniacal brines are shown in Fig. 2.[1] At low values of the bicarbonation

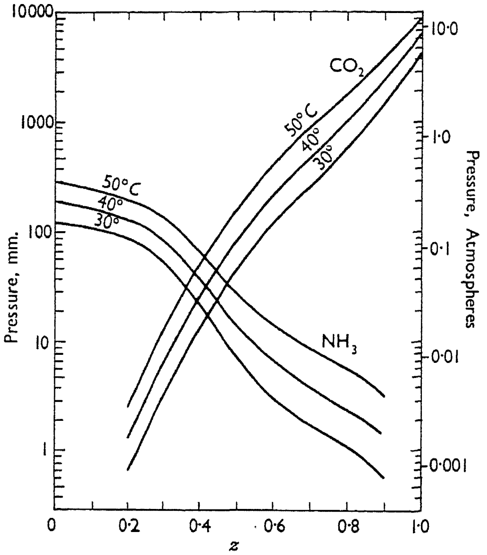

FIG. 2. PARTIAL PRESSURES OF CARBON DIOXIDE AND AMMONIA OVER CARBONATED AMMONIACAL BRINES

index z (see below) p_{NH_3} is high, but p_{CO_2} is very low; at complete carbonation p_{CO_2} is very large. At the top of the carbonating towers $z \simeq 0{\cdot}4$, and the highly ammoniacal incoming brine is a good scrubbing agent for carbon dioxide. The exit gases contain appreciable quantities of ammonia which must be scrubbed out by fresh brine. The concentration of carbon dioxide in the entering gas should be as high as possible to overcome the back pressure of carbon dioxide in the liquor. The conditions in a carbonating tower are fully examined in Deutsch and MacMullin's Fig. 18.[1]

Analyses of samples taken from various parts of the carbonating tower together with photomicrographs of the crude bicarbonate are available.[21,22]

The tower crystals are highly twinned, differing markedly in appearance from ordinary pure sodium bicarbonate. The towers are operated so as to produce as large crystals as possible, the crystal form being best when the maximum temperature allowed in the tower is about 55°C. Good bicarbonate crystals are granular like sand to the feel, not sticky like starch paste. In some plants the Honigmann equipment of five inverted pear-shaped steel vessels is used, worked in counter-current series; they produce good coarse crystals but require more labour, although not nearly as highly skilled. Because of the necessity of cleaning out in the continuous-flow process and of opening up manholes for raking out scale and inspection, the smallest number of towers possible is three, the maximum five. Hence, the smallest plant which will work efficiently has a minimum daily output of 100 to 150 tons of soda ash.[2] The large tower may conveniently be replaced by a series of relatively small towers equipped with agitators, the ammoniated brine flowing under gravity from the first to the others in succession. Carbon dioxide moves in countercurrent, additional gas being added on the way. The process is said to minimise sedimentation and scaling, and gives large crystals. It may be operated efficiently at 10% capacity.[23,24] Some advantages are claimed for a first carbonation by a low-test carbon dioxide without material precipitation of bicarbonate, and a subsequent treatment by high-test carbon dioxide, the bicarbonate formed being calcined to give soda ash and the high-test carbon dioxide.[25]

An attempt at reducing the complexity of operation suggests cooling a mixture of 2 moles of ammonia per mole of carbon dioxide with rather less than 1 mole of water vapour, until all the ammonia has combined to form carbonate or carbamate, dissolving the solid product in saturated brine and carbonating to precipitate the bicarbonate. This is then calcined and recovered carbon dioxide and ammonia are recycled.[26]

Many patents have been taken out for adjustments in this section of the process by altering the concentrations of the constituents at certain stages or by adapting it so that it may even become an accessory to the industrial ammonia process.[27] Many of the patented processes are in effect two-stage cyclic ones and the necessary ions are circulated between a bicarbonate-producing stage and an ammonium chloride stage.[28] The crystalline ammonium chloride may be made into a slurry with an inert, thermally stable organic liquid, and mixed with a fused bisulphate to remove hydrogen chloride; ammonia is then obtained by stripping.[29]

The action of ammonia and carbon dioxide on a sodium salt in the presence of a soluble salt of an amine has been proposed (e.g. sodium chloride, trimethylamine chloride or a methyl-ammonium nitrate and ammonium chloride) for the preparation of the bicarbonate.[30,31] The solution circulating in the cycle may contain ammonium nitrate and various amine hydronitrates.[32] When carbon dioxide-containing gases are bubbled through an aqueous solution of sodium chloride and *iso*propylamine a 95% yield of bicarbonate is obtained when the carbon dioxide content of the exit gas is increased to 35%. The use of liquid carbon dioxide and ammonia is suggested at temperatures at which the carbamate is no longer stable;[33] the carbon dioxide may be obtained from flue gases and the ammonia by the action of lime on gaseous ammonium chloride, the expansion of the gases being used to absorb heat where needed in the process.[34] Both the bicarbonate and ammonium chloride may be prepared in good yield from sodium chloride, ammonia and carbon dioxide in solution by two cycles of operations, one with the addition of carbon dioxide at 20–40°C. to crystallize the bicarbonate and the other at at least 10°C. lower with more sodium chloride and ammonia to crystallize ammonium chloride.[35,36] A Japanese process employs a hydroxyl exchange resin in carbonated brine to form a mixture of carbonate and bicarbonate, the solution then being concentrated and carbon dioxide passed in to precipitate bicarbonate; the resin is regenerated with gaseous ammonia to form ammonium chloride.[37]

The removal of the precipitated bicarbonate is achieved largely by one of two methods; by rotary vacuum filters (invented specifically for this purpose and presumably still the best device) or by continuous centrifugals. During filtration the bicarbonate crystals are carefully washed to minimise the sodium chloride content. The moisture content is a factor in the behaviour of the bicarbonate in the drying operation. The composition of a typical filter product is $NaHCO_3$ 69·28, Na_2CO_3 7·76, NH_4HCO_3 3·45, NaCl 0·26, $MgCO_3$ 0·17, Na_2SO_4 0·10, H_2O 18·98%. The carbonate appears to arise from the rapid loss of CO_2 on exposure to the air.[2] It is important that the crystals obtained are readily filterable, and for this purpose they should not be too small. Indeed a Russian patent was granted for obtaining large crystals by inoculation with bicarbonate crystals in the carbonation tower.[38] The success of this stage in the process depends upon adequate control of the carbonation and precipitation operations. If this is lacking a mushy filtercake with high salt content, low filter capacity and high fuel consumption in the subsequent stages is obtained. Apparently skilled operators can produce good crystals in almost any type of precipitation equipment.[1]

The wash liquors may be treated with bittern containing magnesium salts to precipitate basic magnesium carbonate, the filtrate with the ammonium salts being recycled.[39]

Many patents[39] exist for the partial or complete modification of this stage. A French specification separates bicarbonate from ammonium chloride by a foam flotation operation, the agent being an aldehyde, in particular heptaldehyde; the bicarbonate is carried away and the ammonium chloride remains in suspension in the saturated solution.[40] A United States patent proposes a continuously operating evaporating tower through which the solution containing ammonium and sodium chlorides, ammonium carbonate, etc. is passed upwards at a gradually decreasing temperature; the salts which deposit at different temperatures are separately removed.[41] Mathematical equations have been devised for calculating the most efficient form of carbonation apparatus, and the carbonating tower is said to be best.[42]

Many devices are in use in different plants for transferring the bicarbonate to the calcining tower or to storage; the free ammonia present makes anything but mechanical transfer extremely difficult and arduous.

Step 4. Decarbonation.

After removal of the bicarbonate the molten liquor goes to the decarbonating stills. It contains ammonium chloride and some sodium bicarbonate; it is heated close to the boiling temperature when the reaction in (3) is reversed, part of the original ammonia (the 'free' ammonia) and all the carbon dioxide - apart from uncontrollable losses - being released ($NaHCO_3 + NH_4Cl \rightarrow NaCl + NH_3 + CO_2 + H_2O$). The residuum contains salt and ammonium chloride (the 'fixed' ammonia).

Step 5. Ammonia Recovery.

The lime obtained in Step 1 is added as a 'milk' to the brine and ammonia distilled off in the stills ($2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + H_2O$). The mother liquor from the bicarbonate should contain nearly all the ammonia with which the brine was originally saturated; the remainder is in the calciner gas condensates and the absorber muds, etc. The stills are often some 200 ft. high. The composition of the distiller waste varies considerably but an average sample might have a sp. gr. of 1·10–1·13 and contain the following (concentrations in g. per l. of waste): $CaCl_2$ 85–95, NaCl 45–50, $CaCO_3$ 6–15, $CaSO_4$ 3–5, $Mg(OH)_2$ 3–10, CaO 2–4, Fe_2O_3 and Al_2O_3 1–3, SiO_2 1–4, and NH_3 0·006–0·012. There is also a large quantity of solids in suspension. The data are provided by Hou,[2] who points out their importance as a 'barometer' marking the conduct of the whole ammonia-soda process; it is possible to check the efficiency of many of the stages. Thus low specific gravity will indicate a large volume of feed liquor to be distilled with consequent high consumption of steam and coal, and greater ammonia loss; low calcium/sodium ratio indicates low conversion in carbonation and wastage of sodium chloride; undue presence of ammonia indicates heavy loss through the distiller;

high lime content indicates an unnecessarily large excess of milk of lime and high consumption of limestone and so on. It has been stated that in a modern plant 0·3 to 0·4kg. of ammonium sulphate are lost per 100kg. of product.[4]

The disposal of the waste is one of the major difficulties of the process. Refined common salt may be prepared from it, and clarified calcium chloride liquor (42–45%), known as 'liquid calcium chloride' may be shipped in tank cars for refrigerating plants, road sprinkling, and liquid concrete accelerators, or for conversion into solid flaked or anhydrous calcium chloride. Small quantities are absorbed as catalysts in the manufacture of cyanamide.

The waste liquor may be treated with the sludge from the earlier refining of the brine to give calcium carbonate and a solution of magnesium chloride which may in turn give hydrogen chloride and magnesia.[43] Japanese patents also exist for the treatment of waste distiller liquor by a sodium cation-exchange resin to convert calcium chloride into sodium chloride.[44]

Ammonia may be liberated from the ammonium chloride by treatment with an alkaline-earth sulphide and conversion of the resulting ammonium sulphide into ammonia by means of alkali; feeder liquor from the bicarbonate filters is heated and decomposed, barium sulphide from a black ash is introduced. Barium chloride and ammonium sulphide are formed, the latter giving sodium sulphide and free ammonia with sodium hydroxide or sodium carbonate.[45] An interesting set of analyses of waste still liquor from a number of different works was made some time ago. It is difficult to say whether the results are significant today: the wide variation would suggest that some of the works can no longer be active, e.g. sp. gr. 1·047 to 1·113, NaCl 22·42 to 70·50, $CaCl_2$ 35·70 to 110·80, NH_3 0·0064 to 0·0201 (all in g./l.)[46]

Step 6. Ammonia Absorption.

The ammonia from Steps 4 and 5 is absorbed by fresh brine in the absorbers, the cycle thus being completed ($NaCl + H_2O + NH_3 \rightarrow NaCl + NH_4OH$).

Step 7. Calcination of Bicarbonate.

The crude sodium bicarbonate from Step 3 contains about 5 mol.-% of ammonium bicarbonate in solid solution. As such its uses would be severely restricted: it is therefore calcined to soda ash in the calciners. ($2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$; $\Delta H = 30{,}600$ g.-cal.; $NH_4HCO_3(s) \rightarrow NH_3(g) + CO_2(g) + H_2O(g)$; $\Delta H = 44{,}200$ g.-cal.). The dissociation temperature of dry sodium bicarbonate is 102°C. and that of sodium carbonate monohydrate, 105°C.; the reaction is carried out in the range 175–190°C. in indirectly fired rotary furnaces, generally in a preliminary drying operation followed by a finishing calcination. The calciner gases are cooled and scrubbed to remove ammonia; the resulting gas which is compressed and recycled contains about 97% of carbon dioxide. $p_{CO_2} \cdot p_{H_2O}$ must be a constant at a given temperature (0·23 atm.^2 at 100°C.). The technique of fluidization has been applied to the calcination; the bicarbonate is decomposed by heat in a rising stream of carbon dioxide, air, and steam in a fluidized bed of carbonate; two beds are used with saturated steam at different temperatures and pressures, the hot carbonate being cooled in a bed of predried carbonate fluidized by dry air or carbon dioxide. Slightly hydrated low-density carbonate may be densified by decomposition in a heated fluidized bed of dense carbonate.[47–49]

Wet calcination has certain advantages in heat economy since $2NaHCO_3$ (aq.) = Na_2CO_3 (aq.) + H_2O (l.) + CO_2 (satd. soln.); $\Delta H = 250$ g.-cal., the heat effect being negligible; heat is, however, required for the solution of bicarbonate, and to drive carbon dioxide out of solution.

This process may therefore provide soda solution for causticization, or refined sodium bicarbonate or sesquicarbonate. For the latter a slurry of about 520 parts of crude bicarbonate to 1000 parts of water is heated until

78% of the bicarbonate is converted to soda ash, and transferred to a crystallizing tank to allow the characteristic needles to form.

Step 8. Densification.

The sodium carbonate from Step 7 is loose - a 'light soda-ash'. For many purposes it must be densified; usually sufficient water is added to give the monohydrate in largish crystals which are dehydrated to form dense ash in the densifiers or rotary driers at 135–155°C. Soda ash contains about 99·4% of Na_2CO_3, 0·0% of $NaHCO_3$, 0·18 to 0·33% of NaCl, and about 0·25% of water. The density of 'light ash' loose varies from 0·38 to 0·52; packed about 0·81 g./c.c.; that of 'dense ash' is 1·23 g./c.c. The heating of Wegscheider's salt, $Na_2CO_3,3NaHCO_3$, also gives a bulky ash.[51] Other forms for specialized use are 'extra light' (23 lb. per cu.ft.) which is generally collected from points of sedimentation of soda-ash dust in alkali factories, 'fused' which is the product of melting in an open-hearth furnace for metallurgical processes, and 'pressed', formed in hydraulic presses to minimize container costs and shipping space. It may also be briquetted under high pressure.[52]

'Modified sodas' are various mechanical mixtures of sodium carbonate and bicarbonate containing from 25 to 75% of bicarbonate.

A dense ash may be produced by crystallizing anhydrous soda from a saturated aqueous solution above the transition point of monohydrate–anhydrous carbonate at the same time maintaining in the solution 0·1 to 1% of bicarbonate which helps to give larger and better formed crystals.[53] Patents exist for the crystallization of dense soda-ash from solutions containing caustic soda substantially in excess of that resulting from the hydrolysis of sodium carbonate,[54] the transition point of the monohydrate being lowered either by addition of other substances or by increasing the external pressure.[55,56] High-density ash may also be obtained by partial hydration in the presence of aryl sulphonates.[57] The monohydrate may be produced by precipitation from soda solution by adding ammonia.

The technique of evaporation by submerged combustion may be applied to solutions of sodium carbonate and sulphate. Both have transition temperatures at about 32–35°C. and inverted solubility curves above the transition point; the stable phase for the carbonate is the monohydrate, the sulphate being anhydrous. The process is carried out at about 90°C. and avoids the formation of scale on the evaporator body.[58] True scale is formed only when an inverted solubility curve is present. The evaporation can be performed only with difficulty in ordinary apparatus.[59]

The separation of sodium carbonate and sodium chloride may be achieved by control of particle size during evaporation and crystallization followed by sieving or elutriation with an inert liquid. The particle size is controlled by seeding, or by adding supersaturated solutions or small amounts of colloids like gelatin.[60]

There are many other patents associated with the later stages of the process, such as recovering precipitated salts from solutions of carbonate or sulphate,[61] or drying solutions to give a hardened product.[62] To aid the formation of very hard crystals of the decahydrate, crystallization may be induced in the presence of 4–6% of sodium sulphate. After clarification with alum or bleach the crystallization takes 8–14 days; the crystals have to be removed with hammer and chisel. Fine crystals are had in a mush by agitation and by keeping the walls free from crystals.[63]

Step 9.

Carbonating towers are again employed in recarbonating soda solution to precipitate pure sodium bicarbonate: $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$. Since the refined bicarbonate is used pharmaceutically or in the baking trade it is necessary to have a high-grade carbon dioxide in the process. For baking powder minor amounts of starch, sodium phosphates, etc. are added to ensure a free-flowing product.[66]

There are many patents for refining the crude bicarbonate as it comes from the filters, although the usual method is to recarbonate a soda solution. One successful process involves dissolving the crude bicarbonate hot, distilling off ammonia, and recarbonating the partially decomposed bicarbonate. The same method has been used in the preparation of soda liquor for causticization. Bicarbonate in a very fine state of division is obtained by suspending soda ash or the monohydrate in a water-soluble organic liquid in which the suspended particles are insoluble and then carbonating below 40°C.[64] The absorption of carbon dioxide by solid hydrated soda is practically possible if the hydration is performed immediately before use; increase in hydration or addition of solid bicarbonate increases the velocity of absorption.[65]

So made the bicarbonate analyses $NaHCO_3$ 99·80–99·92, NaCl 0·10–0·20%, with a trace of ferric oxide.

A useful empirical equation derives from the equilibrium study of the system Na_2CO_3-$NaHCO_3$-CO_2 in water. It is $x^2Cl^{1\cdot 29}/SP(1-x)(185-t) = 10$ where C = concn. of Na^+ (equiv./l.); t = temperature of solution (°C.); S = solubility of carbon dioxide in water at t° and 1 atm. partial pressure in g.-mol./l.; P = partial pressure of carbon dioxide above the solution; and x = fraction of Na^+ existing as bicarbonate. It holds for values of C between 0·5 and 2·0 N. for a temperature range of 20° to 70°C., and for partial pressures of carbon dioxide up to 1 atm., but fairly certainly higher.

Step 10.

Finally some soda ash is causticized with lime; the precipitated calcium carbonate $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$, is removed, dried, reburned and hydrated to lime for Step 5 and the above. Caustic alkali plants are usually run in conjunction with soda manufacture. (See section on Utilization).

Equilibria in the Ammonia-Soda Process

The following account of the equilibrium conditions in the process is adapted with little change from Deutsch and MacMullin.[1]

Heterogeneous Equilibrium.

In the five-component system $Na_2{}^+$-$NH_4{}^+$-Cl^--OH^--$HCO_3{}^-$-H_2O the isothermal and isohydrol conditions are most satisfactorily displayed by a triangular prism; the composition of any mixture of the components being represented by the location of a point $P(x,y,z)$ within or on the boundaries of the prism: the variables x = cation index = $NH_4{}^+/(Na^+ + NH_4{}^+)$, y = anion index = $(OH^- + HCO_3{}^-)/(Cl^- + OH^- + HCO_3{}^-)$, z = bicarbonation index = $HCO_3{}^-/(OH^- + HCO_3{}^-)$, and h = water index = $H_2O/(Na^+ + NH_4{}^+)$. Points within the prism are non-variant with respect to temperature and are water-free. It is therefore necessary to supplement the information $P(x,y,z)$ with the value of h corresponding to the point giving $P(x,y,z,h)$. This will give a series of isothermal isohydrols on the equilateral triangular sections which correspond to the pseudo-ternary systems involved, and on the quadrilateral faces which give the pseudo-quaternary equilibria. The significance of the ionic indexes or ratios will be apparent from Figs. 3, 4 and 5, which show respectively the complete system, the system $NaOH$-NH_4HCO_3-NH_4OH-$NaHCO_3$, and the system $NaCl$-NH_4OH-NH_4HCO. The 'mixture law' as usual holds for this representation and the composition of any mixture of two constituents is represented by a point on the line joining them. For this purpose to avoid undue complications all sides of the prism should be equal and in that sense Fig. 3 is distorted; Fig. 4 is the base of the prism, and Fig. 5 is one of the end faces. The figures are taken from Thorpe.[1] These additional sections

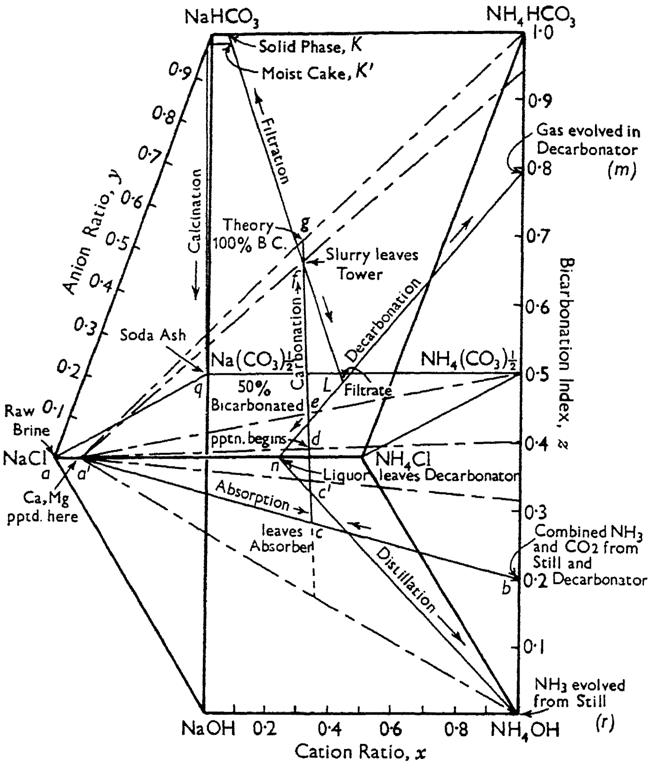
NaHCO$_3$
NH$_4$HCO$_3$
Solid Phase, K
Moist Cake, K'
Filtration
Calcination
Theory 100% B C.
g
Slurry leaves Tower
f
Carbonation
Decarbonation
Gas evolved in Decarbonator (m)
Soda Ash
Na(CO$_3$)$_{\frac{1}{2}}$
NH$_4$(CO$_3$)$_{\frac{1}{2}}$
50% Bicarbonated
q
L
Filtrate
e
pptn. begins
d
Raw Brine
NaCl
a
a'
Ca, Mg pptd. here
n
NH$_4$Cl
Liquor leaves Decarbonator
c'
Absorption
leaves Absorber
c
Distillation
Combined NH$_3$ and CO$_2$ from Still and Decarbonator
b
NH$_3$ evolved from Still (r)
Anion Ratio, y
0·1 0·2 0·3 0·4 0·5 0·6 0·7 0·8 0·9
Bicarbonation Index, z
1·0 0·9 0·8 0·7 0·6 0·5 0·4 0·3 0·2 0·1
NaOH 0·2 0·4 0·6 0·8 NH$_4$OH
Cation Ratio, x

FIG. 3. AMMONIA-SODA PROCESS DIAGRAM

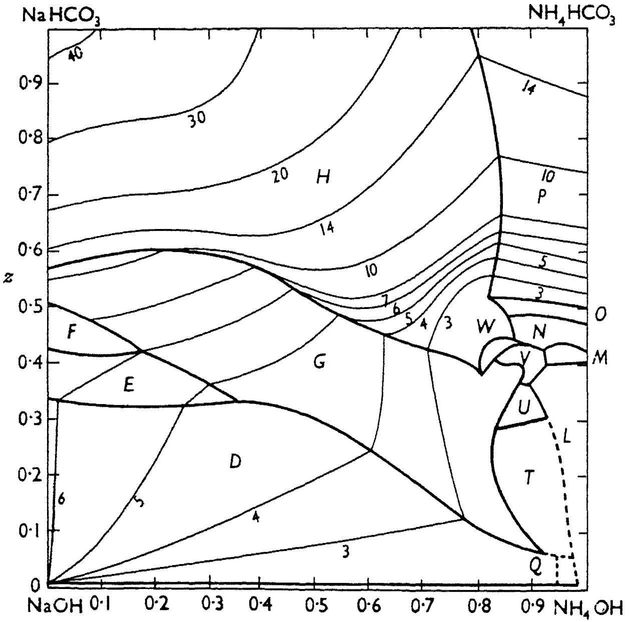

FIG. 4. THE SYSTEM NaOH-NH$_4$HCO$_3$-NH$_4$OH-NaHCO$_3$
TEMPERATURE, 30°C. $\gamma = 100$

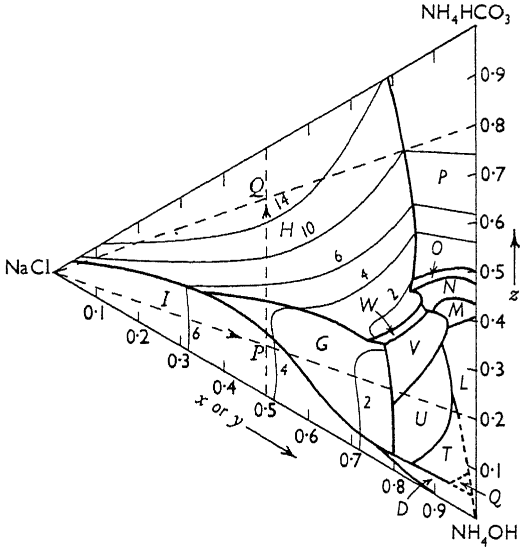

FIG. 5. THE SYSTEM NaCl-NH_4OH-NH_4HCO_3 AT 30°C.
NOTE: *z* CO-ORDINATES RADIATE FROM THE NaCl CORNER

may be found together with examples of the use of the ionic indexes. It will be sufficient here to show how the latter are derived. If normal reagent solutions are used, and SO_4^{2-} is absent, T = total ammonia titre = NH_4^+, B = free base titrable ammonia = $OH^- + HCO_3^-$, F = fixed ammonia = NH_4CL, Cl = chloride titre = NaCl + NH_4Cl, A = molecular carbon dioxide = ½ CO_2 titre = HCO_3^-, CO_3^{2-}. We have $Na^+ + NH_4^+ = Cl^- + OH^- + HCO_3^-$ and therefore $x = T/(Cl + B)$, $y = B(Cl + B)$, $z = A/B$. The yield or percentage decomposition $D_1 = 100F/Cl$. The whole of the ammonia-soda process may be followed from Fig. 3. The compounds occurring in the ammonia-soda system are listed in Table IV.[1]

The symbol in the first column identifies the various fields in Figs. 2, 3 and 4. It is instructive to determine the index formulation of the compounds; for example sodium carbonate in terms of the system components is: $Na_2CO_3 = 2Na^+ + HCO_3^- + OH^- - H_2O$ and in equivalents $Na_2CO_3/2 = Na^+ + HCO_3^-/2 + OH^-/2 - H_2O/2 \therefore x = NH_4^+/(Na^+ + NH_4^+) = 0$, $y = (OH^- + HCO_3^-)/(Cl^- + OH^- + HCO_3^-) = 1$, $z = HCO_3^-/(OH^- + HCO_3^-) = 0{\cdot}5/1 = 0{\cdot}5$, $h = H_2O/(Na^+ + NH_4^+) = -0{\cdot}5$. The sesquicarbonate is $Na_2CO_3,NaHCO_3,2H_2O$ and $x = 0$, $y = (1+2)/(1+2) = 1$, $z = 2/(1+2) = 0{\cdot}67$, $h = 1/3 = 0{\cdot}33$. The mixture of carbon dioxide and ammonia recovered in Steps 4 and 5 is generally about 0·20 (point *b*); if this is passed into rock-salt brine any magnesium and calcium present will be precipitated in a process of 'internal purification' ($CaSO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4$). We may consider the ammonium sulphate as equivalent to ammonium chloride in this small concentration so that although a pure brine would be represented by *a*, the system starts off with a small ammonium content represented by *a′*. On the continued passage of the gas mixture *b*, the point representing the composition, moves along the line *ba′* until it reaches *c*, with the ammonia and salt providing a cation index *x* of approximately 0·5, at which point the ammoniated brine leaves the absorber. It is then carbonated (Step 3) with kiln gas (Step 1) and gas from the calciners (Step 7) and the composition moves along the line *cg*; because of the nitrogen content of the kiln gas some of the ammonia is carried away out of the carbonating towers, and the slight decrease in ammonia content is shown by the slope of the line. At

TABLE IV.- TABLE OF COMPOUNDS OCCURRING IN AMMONIA-SODA SYSTEM

Symbol	Formula	Common name	Composition			
			x	*y*	*z*	*h*
A	NaOH	Sodium hydroxide	0·00	1·00	0·00	0·00
B	$NaOH,H_2O$	Sodium hydroxide monohydrate	0·00	1·00	0·00	1·00
*B*2	$NaOH,2H_2O$	Sodium hydroxide dihydrate	0·00	1·00	0·00	2·00
*B*3	$NaOH,3\frac{1}{2}H_2O$	Sodium hydroxide heptahydrate	0·00	1·00	0·00	3·50
*B*4	$NaOH,4H_2O$	Sodium hydroxide tetrahydrate	0·00	1·00	0·00	4·00
C	Na_2CO_3	Sodium carbonate	0·00	1·00	0·50	−0·50
D	Na_2CO_3,H_2O	Sodium carbonate monohydrate	0·00	1·00	0·50	0·00
E	$Na_2CO_3,7H_2O$	Sodium carbonate heptahydrate	0·00	1·00	0·50	3·00
F	$Na_2CO_3,10H_2O$	Sodium carbonate decahydrate	0·00	1·00	0·50	4·50
G	$NaHCO_3,Na_2CO_3,2H_2O$	Sodium sesqui-carbonate	0·00	1·00	0·677	0·333
H	$NaHCO_3$	Sodium bicarbonate, pure	0·00	1·00	1·00	0·00
H'	$NaHCO_3$	Sodium bicarbonate, solid solution	0·05	1·00	1·00	0·00
I	NaCl	Sodium chloride	0·00	0·00	0·00	0·00
*I*2	$NaCl,2H_2O$	Sodium chloride dihydrate	0·00	0·00	0·00	2·00
J	NH_3	Ammonia, anhydrous	1·00	1·00	0·00	−1·00
K	NH_4OH	Ammonium hydroxide	1·00	1·00	0·00	0·00
L	$NH_4CO_2NH_2$	Ammonium carbamate	1·00	1·00	0·50	−1·00
M	$(NH_4)_2CO_3,H_2O$	Ammonium carbonate monohydrate	1·00	1·00	0·50	0·00
N	$NH_4HCO_3,NH_4CO_2NH_2$	Ammonium bi-carbonate-carbamate	1·00	1·00	0·667	−0·667
O	$2NH_4HCO_3,(NH_4)_2CO_3,H_2O$	Ammonium sesqui-carbonate	1·00	1·00	0·750	0·00
P	NH_4HCO_3	Ammonium bi-carbonate	1·00	1·00	1·00	0·00
Q	$NaCO_2NH_2$	Sodium carbamate	0·50	1·00	0·50	−1·00
R	$NaNH_4CO_3,2H_2O$	Sodium ammonium carbonate dihydrate	0·50	1·00	0·50	0·50
S	NH_4Cl	Ammonium chloride	1·00	0·00	0·00	0·00
*S*3	$NH_4Cl,3NH_3$	Ammonium chloride triammoniate	1·00	0·75	0·00	−0·75
*S*6	$NH_4Cl,6NH_3$	Ammonium chloride hexammoniate	1·00	0·86	0·00	−0·86
*T**	$4NaNH_4CO_3,NH_4HCO_3,4H_2O$		0·56	1·00	0·56	0·00
*U**	Na_2CO_3,NH_4HCO_3		0·36	1·00	0·65	−0·65
*V**	$2Na_2CO_3,NaHCO_3,NH_4HCO_3$		0·13	1·00	0·77	−0·23
*W**	$4NaHCO_3,NH_4HCO_3$		0·19	1·00	0·97	−0·22
X	$(NaCO_2)_2NH$	Sodium carbimide	0·333	1·00	0·666	−1·00

* Approximate formulæ and compositions.

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c', z is about 0·32, the liquor is still unsaturated with respect to sodium bicarbonate, and it dissolves out accumulations of crystals from a carbonating tower which has already been in use for some time, thus 'cleaning' the tower and preventing its blockage. The liquid is then transferred to other or 'making' towers and at d ($z \simeq 0{\cdot}4$) the precipitation of sodium bicarbonate begins. Bicarbonation ceases at point f with the slurry about 95% bicarbonated, 100% being g. The solid phase in the slurry is sodium bicarbonate with about 5% ammonium bicarbonate in solid solution (k in Fig. 3), the solution in equilibrium being l. After filtering and washing the bicarbonate still contains some chloride in addition to the ammonium salt and the moist solid phase is now k'. The filtrate is about 80% bicarbonated (z = 0·8); it goes to the decarbonating still (Step 4) and the recovered gas is point m in equilibrium with the decarbonated liquor n. The latter is treated with lime (Step 5); the liquid phase now contains calcium ion and cannot therefore be accommodated in Fig. 3, but the recovered ammonia can be represented by NH_4OH at point r. Finally the crude bicarbonate k' is calcined (Step 7); ammonia is first eliminated leaving sodium bicarbonate p, followed by carbon dioxide giving soda ash q.

This account of the equilibrium conditions in the process is, as emphasized earlier, based on the exhaustive work of Deutsch and MacMullin. There are a number of other investigations to which brief reference might be made.

Equilibria in the reaction $NaCl + NH_4HCO_3 \rightleftharpoons NH_4Cl + NaHCO_3$ have been studied at 15°C.[67] and at 35° and 50°C.[68] The composition of the solutions in equilibrium with various solid phases are given.[69]

Carbonation of aqueous ammoniacal suspensions of sodium chloride and sulphate (for the same Na^+ concentration the following properties are said to be additive and independent of the SO_4^{2-}/Cl ratio: composition of solution after carbonation, proportion of combined ammonia, degree of ammonia and sodion utilization, and density). The process is said to be complete in 3–4 hr. with 75% sodium conversion.[70]

The kinetics of the crystallization of sodium bicarbonate have been explored in the Russian general examination of the ammonia-soda process;[71] in the initial stages the rate of absorption of carbon dioxide is a maximum at 60°C., the temperature of maximum rate dropping with the bicarbonation index to 30°C. at $z \simeq 0{\cdot}80$. Intensive crystallization at any rate of carbonation begins at pH = 10 and $z \simeq 0{\cdot}55$. The rate of crystallization from supersaturated solution is proportional to the cube of the degree of supersaturation, which decreases with rise in temperature and fall in carbonation rate.

The equilibria at high pressures (50 atm.) of carbon dioxide have been investigated by Japanese workers; the final equilibrium under high pressure is established as $NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl$ each of which substances is a possible solid phase.[72]

In a laboratory examination it appears that when carbon dioxide is passed into aqueous ammonia only carbamate is produced, the latter gradually hydrolyzing to ammonium bicarbonate on reaching a definite concentration. The greater the ammonia concentration, the carbon dioxide content remaining the same, the greater is the carbamate formation and the higher the ratio of carbamate to bicarbonate at equilibrium. The more carbon dioxide present, the more rapidly formed and the larger is the precipitate when definite quantities of sodium chloride are added. Complete transformation of carbamate to bicarbonate cannot, however, be obtained by intensifying the flow of carbon dioxide.[73,74]

Furthermore, on the proposition that the composition of the solution is determined by its temperature, vapour pressure and chloride ion concentration, empirical equations have been devised giving the concentrations of sodium chloride and ammonium ions, alkali, carbon dioxide and water and found to hold at 15°, 20° and 30°C. and vapour pressures of 0·5, 1, 2 and 3 atm. The results of variations in component concentrations are described.[75]

The influence of concentration of brine, temperature, partial pressure of ammonia, concentration of carbon dioxide in solution and in the gaseous phase, has been studied. High ammonia concentrations have favourable influence on the speed of carbon dioxide absorption.[76]

Vapour pressure and content in the gas phase above the salt solutions have been determined; undissociated ammonium carbamate is said to be present in the gas phase but it begins to dissociate strongly above 30°C., dissociation being complete at 40°C. At 25·9°C. and p_{CO_2} = 1·2 atm., sodium bicarbonate and ammonium chloride exist alone in solution; at lower temperatures sodium chloride is present, at higher there is ammonium bicarbonate. At p_{CO_2} = 2·5 atm., the corresponding temperature is 27·8°C.[77]

Modifications of the Solvay Process

Liquid Ammonia.

At the boiling point of liquid ammonia the solubility of sodium chloride in ammonia is very low, and $NaCl,xNH_3$, instead of NaCl, is the stable form in contact with the solution. From about −10°C. up to room temperature the solubility of sodium chloride is fairly great, NaCl being the stable, solid phase although the temperature coefficient of solubility is negative. Magnesium and calcium chlorides and sulphates (the customary impurities) are insoluble in liquid ammonia, so that purification may be effected. When carbon dioxide is passed into a liquid ammonia solution of sodium chloride above −10°C., an exothermic reaction occurs, $NaCO_2NH_2$ being precipitated in 99% yield. Steamed at 100–300°C. this yields ammonia and sodium carbonate.[78] A scheme has been devised for the analysis of the mixtures obtained in this process, which may include ammonium and sodium carbamates, ammonium and sodium chlorides, and free ammonia.[79]

The 'closed circuit' processes are based on the use of an intermediate conversion agent and form the subject of many patent specifications; we even find magnesium hydroxide in one case.[85] A saturated solution containing $NaCl,|NH_4Cl,|NH_4HCO_3$ (or $NaHCO_3$) and a readily soluble sodium salt (e.g. nitrate) or a soluble thiocyanate (e.g. ammonium) or a mixture of readily soluble sodium or ammonium salts, is treated with ammonia and carbon dioxide; sodium bicarbonate is precipitated and the filtrate, without evaporation or cooling, is treated with sodium chloride to precipitate ammonium chloride. The presence of the readily soluble salts mentioned prevents simultaneous precipitation of bicarbonate and ammonium chloride.[80-84] The use of substituted amines e.g. $(CH_3)_3N$ has been patented.[86]

The Claude process treats salt and gaseous ammonia, dissolved in a mother liquor of ammonium carbonate and ammonium chloride, with pure carbon dioxide under pressure. The sodium bicarbonate is removed; the mother liquor is treated with ammonia to convert ammonium bicarbonate to carbonate and ammonium chloride is separated at atmospheric temperature. The process is repeated.[87]

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OTHER METHODS OF SODA MANUFACTURE

Many patents have been assigned to the production of the carbonate and bicarbonate by processes other than ammonia–soda.

Deutsch and MacMullin cite some twenty-two methods by which sodium carbonate may be made. It is not necessary to repeat this summary since its contents are matters of historic interest, many of them indeed dating back to the eighteenth century and already included in Mellor, Vol. II. The Le Blanc process disappeared shortly after the First World War; its products were impure, it was expensive and complicated to run, it required a large labour force and the wastes were notoriously difficult to dispose of. It will be seen from the following account that much work has been done upon the use of sodium sulphate in the place of sodium chloride, and to that extent a half-way stage in the Le Blanc process has been adapted with some success in countries where large quantities of sodium sulphate occur naturally, particularly in Asia. The sodium carbonate may not be isolated, but on occasions is converted directly into caustic soda.

The Penjakow Process.

This is based on the reactions $4Al_2O_3 + 4Na_2SO_4 + 2C \rightarrow 8NaAlO_2 + 4SO_2 + 2CO_2$ and $2NaAlO_2 + CO_2 \rightarrow Al_2O_3 + Na_2CO_3$. The first reaction occurs at a bright red heat and the second in water at ordinary temperatures. The usual procedure however of agitating the aluminate solution with freshly precipitated aluminium hydroxide is followed, and after 24–36 hr. some 80% of the aluminium is thrown down as $Al(OH)_3$ in a readily separable form; the remainder is removed by treatment of the solution with slaked lime, $2NaAlO_2 + Ca(OH)_2 \rightarrow 2NaOH + Ca(AlO_2)_2$. The alkali is concentrated as usual, and the $Ca(AlO_2)_2$ precipitate decomposed by boiling with soda under pressure. The sodium aluminate formed is then decomposed with carbon dioxide, and the aluminium hydroxide returned to the process.[5]

A French patent proposes the calcination of clay briquets which are then treated with 'sulphuric acid, water, steam and air, sulphur dioxide and trioxide' to produce a product with a high aluminium sulphate content. The briquets are leached with sulphuric acid and water and the aluminium sulphate so obtained is dehydrated and partly dissociated. The resulting mass is briquetted with salt and coal and treated at a red heat with superheated steam. Subsequent leaching gives pure alumina and sodium carbonate.[6]

Sodium Carbonate Production from Industrial Wastes.

Strong acid wastes from the production of titanium oxide contain as much as 8·5% H_2SO_4 and 11% $FeSO_4,7H_2O$; they are neutralized with caustic soda, and the precipitated ferric hydroxide heated to form ferric oxide. The filtrate is treated with lime to give $CaSO_4,2H_2O$ and sodium hydroxide. The calcium sulphate is converted, after filtration, into plaster of Paris; the filtrate is partly recycled and partly converted into sodium carbonate. 1 gallon of waste produces about 4·5 oz. of ferric oxide, 2 lb. of $CaSO_4,2H_2O$ and 1·1 lb. of soda ash.[7]

Production of Sodium Carbonate from By-Products of Wood Pulp Manufacture.

Black Liquors.

Residual solutions containing sodium carbonate and sulphide are treated with sulphur dioxide to give hydrogen sulphide and sodium bicarbonate.[98] The organic matter present may be precipitated by adding magnesium bicarbonate. The filtered liquid is boiled, the carbon dioxide recovered, and the resulting sodium carbonate causticized. The organic matter may be burned or distilled to give acetic acid, alcohol and acetone.[8]

The heat of combustion of the organic matter may be used to effect concentration of the liquors: an initially concentrated liquor is atomized in a combustion space previously heated to start combustion. Soda ash collects and is recovered.[9,10]

The 'black liquor' is 'spent cooking liquor' in the sulphite process. It gives black ash on evaporation and carbonization. A good recovery of soda can be obtained only if an adequate proportion of black liquor is forthcoming at a strength and volume which can be efficiently dealt with. The factors affecting this and the efficiency of the evaporator have been fully discussed.[11]

Comparative values for the heat balance in soda recovery from black liquors are available.[13]

The ash may be treated with a mixture of air and steam at a temperature to effect combustion of a part of the carbon content; this treatment converts the sodium sulphide to carbonate and eliminates hydrogen sulphide. The resultant ash is dissolved in water to obtain soda free from sulphide.[12] In one patent the non-combustible part is led in to form a layer on the interior walls of the furnace and acts as a refractory.[20]

Waste Sodium Monosulphite Liquors.

Many patents exist for treating these; they may be concentrated and burnt in the presence of air, sometime after treatment with calcium carbonate. Sodium carbonate is formed together with calcium sulphide. The former is reconverted to the monosulphide, and the latter decomposed by carbon dioxide to liberate hydrogen sulphide, which is burnt to sulphur dioxide.[14-18]

In the Sulfox process, sodium is substituted for calcium in the sulphite cook. The spent liquor is evaporated and burned, yielding a smelt of sodium sulphide and sodium carbonate. The smelt is dissolved and the sodium sulphide is air-oxidized to give sodium sulphite. The sodium sulphite and sodium carbonate are combined with recovered sulphur dioxide to give make-up acid for cooking.[22] Patents exist for the fusion furnaces required in this operation.[24,25] It is also stated that the smelt dissolved in water yields NaSH and NaOH, and may be carbonated to give a mixture of NaSH and $NaHCO_3$.[26] Pressure carbonation may be followed by vacuum steam distillation to remove hydrogen sulphide.[23] If the waste sulphite liquor is carbonated directly, it forms a viscous liquid the filtrate from which gives aqueous soda and hydroxide for causticization, the residue containing polyphenols and glycerides.[19]

The inorganic content of spent pulp-cooking liquor is melted in a reducing atmosphere to produce sodium carbonate and sulphide, the hot melt being run into water and cooled to crystallize the carbonate; the mother liquor is used for the production of fresh cooking liquor.[27-29] If the sodium carbonate is to be causticized, the major portion of the sodium sulphide may be removed by discharging the smelt into strong sodium sulphide solution, in which the carbonate is not very soluble. Thus a neutral sulphite green ash of composition (in mol.-%) Na_2S 37, Na_2CO_3 59, Na_2SO_4 4, if added to a 1:3·5 aqueous solution of sodium sulphide at about 90°C. has all the sulphide removed, 35% of the sulphate and 10% of the carbonate.[21] The smelt causticized with lime is known as *greenlime*: it contains precipitated calcium carbonate and small amounts of sodium carbonate with the sodium hydroxide. After treatment with exhaust gases from the digesters and the smelting furnaces it contains sodium carbonate, sulphide, sulphate, thiosulphate, and sulphite, and hydrogen sulphide, with a number of organic compounds, which may be separated.[30]

The 'green liquor' obtained from the ash as above may be carbonated to form sodium bicarbonate which is sulphited to sodium sulphite to be incorporated in the original process.[31]

The waste lye from the sulphite process may be concentrated, mixed with alkali or calcium salts, and evaporated. The residue contains carbon and if heated to 1000°C. gives sodium carbonate, calcium sulphide, and oxide, which are worked up.[32]

The soda ash aerosol formed in the burning of black liquor in paper mills may be agglomerated by subjection to sound waves of at least 140 decibels and approximately 1000 cycles per second.[33] The aerosol is responsible for considerable stack losses if untreated; it can be passed through a Cottrell precipitator. In one comprehensive test on a furnace operating on black liquor from a 105 ton soda-pulp mill, the dust leaving the furnace amounted to 304 lb. of Na_2CO_3 per hr., equivalent to 4·4% of the chemical input to the furnace. The precipitator removed 87% of the escaping carbonate, worth $57 per day in 1939.[34]

The waste soda solutions from viscose manufacture may be purified by treatment with carbon dioxide; the temperature rises and facilitates the separation of precipitated organic substances, and after filtration and cooling sodium bicarbonate is crystallized.[35]

Production of Sodium Carbonate from Sodium Sulphate etc., by Resin Exchange.

2 N. Ammonium bicarbonate solution was passed at a rate of 10 c.c./min. through a column of 100 c.c. of '*Permutit Q*' (cation exchanger) which had been treated with sodium chloride solution: 240 c.c. of 1·4 N. sodium bicarbonate solution were obtained. The resin was regenerated with 800 c.c. of 1·7 N. sodium sulphate solution giving 400 c.c. of a solution containing $(NH_4)_2SO_4$ 0·42–0·46 and Na_2SO_4 0·27–0·35 mole/l. These components were separated by alternate heating and cooling.[36]

Sodium ion may be taken up by 1 kg. of anion-exchange resin from 4 l. of sea water, the solution then being passed through 0·5 kg. of cation exchange resin. 650 ml. of water containing 29% $(NH_4)_2CO_3$ and 3·5% Na_2CO_3 pass through the first resin; washing with 50 ml. water then gives 700 ml. of solution containing 15% $(NH_4)_2CO_3$ and 15% Na_2CO_3. Carbon dioxide passed into this solution gives a precipitate of 120 g. of sodium bicarbonate. The filtrate is cooled and ammoniated to give ammonium carbonate for recycling.[38]

Sea water after freeing from magnesium and calcium may be concentrated in sodium chloride by an involved exchange-resin treatment which utilizes calcium chloride obtained during the process: the brine may be converted into aqueous sodium bicarbonate by treatment with hydroxyl ion-resin from the earlier stages and with carbon dioxide.[37]

100 g. of resorcinol resin immersed in 0·7% caustic soda solution absorb 9·1 g. of Na^+. In 400 ml. of water saturated with carbon dioxide the resin yields a solution containing 6·5% of $NaHCO_3$.[39]

A Permutit patent exists for treating a zeolite with the solution of an electrolyte, regenerating the zeolite with an excess of a relatively concentrated solution of a volatile regenerating agent, and recovering the excess of the latter for recycling. Sodium carbonate may be prepared by treating ammonium-zeolite with sodium chloride, regenerating with ammonium carbonate and recovering excess ammonium carbonate from the soda solution.[40]

The green liquor from the monosulphite cooking process (see above[23]) may be exposed at 50–100°C. to the action of a cation-exchange resin having active exchange centres in the hydrogen form which are substantially less acidic than sulphurous acid. The weak volatile acids (carbon dioxide, hydrogen sulphide) are evolved and Na^+ is absorbed to the extent of some 85% of that initially present as carbonate or sulphide. The resin is then washed and treated with sulphurous acid to regenerate the resin and produce a solution of sodium bisulphite.[41,42]

A sodium-ion exchange resin treated with sodium and magnesium bicarbonates gives an effluent which is cooled to 0°C. to crystallize sodium bicarbonate.[43,44]

Many changes may be rung on these processes. A typical simple example is the treatment of aqueous magnesium bicarbonate with carbon dioxide and a sodium-ion exchange resin to yield sodium bicarbonate and residual magnesium bicarbonate. The latter may be removed as carbonate by heating the solution to 50°C. and is recycled, the mother liquor giving sodium bicarbonate free from sodium chloride and magnesium ions.[45]

Sodium and potassium chlorides may be separated as the bicarbonates by treating the solution with a hydroxyl-ion exchange resin while carbon dioxide is passed in; the filtrate is concentrated and more carbon dioxide is added to give sodium bicarbonate. The process is repeated with the filtrate to yield potassium bicarbonate. The resin is recycled after treatment with calcium hydroxide.[46]

Reduction of Sodium Sulphate.

One process is a modification of the black-ash process. Anhydrous sodium sulphate is mixed with pulverized coal and watered until the mass 'balls', when it is briquetted. The briquets are heated for 12–16 hr. in a shaft or reverberatory furnace by producer gas until the sodium sulphate content has fallen below 1%. The reduced briquets are subjected to lime-kiln gas with steam. The gases drawn initially from the furnace contain 30–40% of hydrogen sulphide; when this falls to 0·1% the reaction is stopped. The briquets retain their shape and are lixiviated to give 96% sodium carbonate.[47]

An interesting wet process involves sodium sulphate, sodium bicarbonate and barium sulphide. The bicarbonate in granular form is mixed with finely ground sodium sulphate and barium sulphide, and the mixture is added to boiling water. The bicarbonate goes into solution with difficulty but reacts with the nascent sodium sulphide immediately the latter is produced from the barium sulphide. Hydrogen sulphide is eliminated by boiling. Barium sulphide is regenerated from the barium sulphate after removal from the sodium carbonate solution.[48]

Another adaptation of the black-ash process is to treat a mixture of sodium sulphate, coke, calcium carbonate and an iron catalyst with nitrogen at 1050°C. In 90 min. about 70% of the sulphate is converted into sodium cyanide, the rest into carbonate and sulphide. The crude cyanide can be decomposed by superheated steam, giving at 500°C. a 100% yield of carbonate and ammonia. The steamed residue is like black ash except that it contains iron and iron oxide. It can be extracted to yield 90–98% soda ash.[49,50]

Sodium sulphate can also be reduced by carbon monoxide. The laboratory investigation of this reaction provides some interesting results. Carbon monoxide from reduced carbon dioxide was bubbled through water at known temperatures to provide a desired partial pressure of water vapour. The mixed gases, passed over powdered sodium sulphate in a porcelain boat, started to react at 720–730°C. and rapidly at 750°C. Ferric oxide was subsequently used as a catalyst; at 660°C. with $p_{H_2O} = 0{\cdot}3$ atm. maximum reduction of 96–97% occurred (with 85–92% sodium carbonate) in 4 hr.[100] With producer gas containing 7% of carbon monoxide (17% in excess of theoretical requirements) only 15·6% conversion of sodium sulphate occurred; with 9·2% carbon monoxide it was 70% complete, and with 14·6% carbon monoxide (158% excess) reduction reached 93·8% with 88·5% of Na_2CO_3.[100]

The reducing gas may be led into the bath of molten sulphate through a submerged burner, which keeps the mass fused and at the same time leaves sufficient unburnt gas to reduce the sulphate to sulphide. The combustion gases (carbon dioxide and steam) decompose the sulphide giving hydrogen sulphide, which is collected, and sodium carbonate, which remains in the bath.[51]

One of the methods for overcoming the sulphur deficiency in France is to heat a homogenized mixture of sodium sulphate, coke and phosphate rock; this requires only one hour's heating at 1000°C. yielding over 80% of its phosphate as transformed phosphorus pentoxide, which is easily extracted together with some sodium carbonate and metasilicate. In France many industries (viscose rayon, refining of metals, nitric acid) have sodium sulphate of small commercial value as a by-product.[101]

Sodium sulphate, coal and lime are mixed, finely ground and briquetted. These are cyanized by heating to 1000°C. with nitrogen. The product is treated with steam, giving ammonia and sodium carbonate.[53,54] The reducing agent may be hydroxide, oxide or carbonate of calcium, barium or lead giving a melt which can be run into water and carbonated.[105]

Much work has been done on the modified Solvay process to obtain soda and ammonium sulphate from natural sodium sulphate, particularly in Russia where enormous quantities of mirabilite are available.[55-57] Sulphuric acid is used to decompose ammonium carbonate present in a frozen-out solution.[58]

In a semi-commercial scale plant the maximum amount of ammonia used was 0·228 tons per ton of sulphate, and of water 1·85 tons in working with 75–80% carbon dioxide. The average composition of the mother liquor at the above concentrations and a final carbonization temperature 29–30°C. is $(NH_4)_2SO_4$ 21·42, Na_2SO_4 12·32, NH_4HCO_3 5·48, $(NH_4)_2CO_3$ 2·0 and H_2O 58·78%.[59,60,99] The technique is described as one of the most complex forms of the ammonia-soda process.[61] The utilization of sodium sulphate in modified ammonia-soda processes is evidently desirable: during the four months of winter the concentrated brine in Karabugaz bay on the Caspian sea deposits 98% sodium sulphate, which is washed ashore by the waves in tens of millions of tons.[68] The procedure involved in the decomposition of mirabilite by ammonia and carbon dioxide has been described in detail: some 98·5% utilization of the original sulphate is said to be possible.[62,63] The sodium sulphate may be replaced by sylvinitic liquors containing potassium sulphate after treatment with calcium or strontium sulphates.[64,65] The crude salts (kieserite) etc. may be treated with ammonium carbamate in anhydrous liquid ammonia to form potassium and sodium carbamates which yield bicarbonates with water.[66] If sodium carbonate is prepared by this or similar processes it may contain 2–5% or more of sodium sulphite. This can be removed by boiling with manganese dioxide.[102]

When a sodium sulphate solution is treated at 105°C. with carbon dioxide, a maximum amount of sodium carbonate is formed when 70% of the sodium sulphate is decomposed. Any precipitated impurities are filtered off, and more carbon dioxide is passed in to precipitate very pure bicarbonate. Sodium sulphide is also formed, and with carbon dioxide gives sodium hydrosulphide and then hydrogen sulphide.[67]

The presence of sodium chloride appears to favour the utilization of sodium sulphate; the following properties are additive for solutions of the same Na^+ concentration and are independent of the SO_4^{--} to Cl^- ratio: composition of the solution after carbonation, proportion of combined ammonia, degree of ammonia and sodium-ion utilization, and density. Thus from known values for carbonated ammoniacal solutions of sodium chloride or sodium sulphate the corresponding values for mixtures can be calculated.[106]

The relative concentration of carbonate to sulphate in an aqueous solution may be increased by ensuring that it is of such concentration and temperature as to be included in the field of burkeite stability ($Na_2CO_3,2Na_2SO_4$), seeding it with anhydrous sodium sulphate and slowly adding sodium chloride below 50°C. so that much of the pure sodium sulphate is precipitated and removed and the crystallization of burkeite prevented.[69]

A British patent was granted for treating aqueous sodium sulphate with carbon dioxide at 20 atm. at 30°C. until the gas is no longer absorbed. The precipitate of sodium bicarbonate, contaminated with a little sodium sulphate, is removed: the liquor contains sulphuric acid and a little sodium sulphate.[71] A Belgian patent requires the additional presence of an alkaline-earth carbonate in suspension; alkali bicarbonate and alkaline-earth sulphate are formed by metathesis.[72] Other patents include Ba_2SiO_4 which in the presence of carbon dioxide is precipitated as sulphate, separated from the alkali carbonate and reconverted to Ba_2SiO_4 by ignition.[73-75] The combined production of sodium carbonate and sulphuric acid from sodium sulphate is proposed in one of the many Russian papers on this subject. The steps are (a) fusion of the sulphate with charcoal to give sodium sulphide and carbon dioxide; (b) reaction of the sulphide and carbon dioxide of (a) to give soda and hydrogen sulphide; (c) combustion of hydrogen sulphide to sulphur dioxide; (d) oxidation of sulphur dioxide with water vapour to trioxide in presence of a tin-vanadium zeolitic catalyst; and (e) conversion of trioxide to sulphuric acid. The process is estimated to halve the usual cost of production of sulphuric acid.[70,104]

The sodium sulphate may be fused and treated with carbon dioxide and steam, or with materials generating these gases when heated. A small quantity of powdered coke may be added to fused calcined soda and sodium sulphate; super-heated steam and carbon dioxide are blown in. The whole mass eventually becomes soda.[103]

In the production of soda ash from solutions containing both sodium and potassium carbonates, use is made of the double sodium-potassium carbonate in the separation; the solution is evaporated and sodium carbonate is crystallized, then the double carbonate, and after cooling the potassium carbonate. The double carbonate and the mother liquor from the potassium carbonate are recirculated. Crude potash (e.g. from the ash of nuts and plants) may contain 77% of K_2CO_3 and 21% of Na_2SO_4; it is treated with sodium chloride and with sodium sulphate decahydrate to produce crystalline sal soda.[52]

The system Na_2SO_4-NH_4HCO_3-H_2O has been investigated at 15°C. for direct production of bicarbonate.[104] The Honigmann type of carbonator (see Solvay Process) is suitable. The time of carbonation increases to 27–30hr. The mean coefficient of the utilization of sodium ion in the carbonation process is 65·3% and the total efficiency of utilization during the production process is 95·7%. The bicarbonate has the necessary crystal formation for easy filtering. After calcination the sodium sulphate content was 1%.[107] The optimum reaction conditions are variously stated.[57]

Sodium silicofluoride, Na_2SiF_6, may be heated to give sodium and silicon fluorides: the sodium fluoride reacts with calcium carbonate to form sodium carbonate and calcium fluoride; the latter is treated with the silicon fluoride and sulphuric acid to recover H_2SiF_6. A similar reaction may be had with HBF_4.[76]

The phenoxide method has been applied to the production of soda from by-product sodium sulphate solution. The reactions are:

$$(1)\ Ca(OH)_2 + 2C_6H_5OH \rightarrow (C_6H_5O)_2Ca + 2H_2O;$$
$$(2)\ Na_2SO_4 + (C_6H_5O)_2Ca \rightarrow 2C_6H_5ONa + CaSO_4;$$
$$(3)\ 2C_6H_5ONa + CO_2 + H_2O \rightarrow 2C_6H_5OH + Na_2CO_3.$$

The process is most suitable for works which will convert the recovered sodium carbonate into lower-grade caustic. A cheap supply of lime and phenol is required. Nearly all the latter is recovered.[77]

Complex alkali fluorides may be used as intermediates in the production of carbonates and bicarbonates from alkaline-earth carbonates and oxides. Three moles of the carbonate are required for each mole of the alkali carbonate in a two-stage reaction.[80]

More complicated cyclic processes are suggested in this manner for the preparation of a number of substances. The chain of reactions may be:[78,79,108]

$$ZnO \xrightarrow{H_2SiF_6} ZnSiF_6 \xrightarrow{NaCl} Na_2SiF_6 \xrightarrow{heat} SiF_4 + NaF;$$
$$2NaF + CaCO_3 \rightarrow CaF_2 + Na_2CO_3;\quad CaF_2 + SiF_4 \rightarrow H_2SiF_6;$$

or

$$BaF_2 \xrightarrow{\text{superheated steam}} Ba(OH)_2 + 2HF;$$
$$HF + NaCl \rightarrow NaF + HCl;\quad 2NaF + Ba(OH)_2 \rightarrow BaF_2 + 2NaOH;$$
$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O.$$

Calcium cyanamide treated with water in the presence of an alkali-metal fluoride yields a solution which may be separated and heated to liberate ammonia and to form alkali-metal carbonate. The alkali-metal fluoride is prepared from the calcium fluoride formed, and the resulting calcium chloride is treated with ammonia in the presence of water and carbon dioxide to produce calcium carbonate and ammonium chloride. The carbon dioxide used is liberated during the production of the cyanamide from calcium carbide.[81,88]

Alkali carbonates may be obtained by treating sodium sulphate or an insoluble silicate such as feldspar with a gas mixture containing carbon monoxide, with or without steam or inert gas, at 400–900°C. under reduced pressure, accelerators such as ammonia, amines or nitrogen oxides being added to the gases. The reaction is effected in a rotary furnace; if sodium sulphate is used the sulphur dioxide evolved should be withdrawn rapidly and converted into the trioxide to turn alkali chloride into sulphate.[82]

Sodium-containing silicates ground with lime, mixed with powdered coal and strongly heated in the presence of carbon dioxide from flue gases distil sodium carbonate.[83]

Sodium carbonate may be obtained by electrolyzing a solution of sodium sulphate and allowing the acid produced to react with an insoluble carbonate such as that of calcium, barium, or lead, placed below the cathode so that the carbon dioxide formed combines with the alkali generated by electrolysis. The carbon anode may be sited at the bottom of the cell and covered with lumps of the insoluble carbonate through which the sodium carbonate is withdrawn; the product usually contains some caustic alkali. Fresh sulphate solution is introduced below or through the anode.[84]

Several patents have been granted for treating the cathode liquors of electrolytic alkali-chloride cells with carbon dioxide.[1,4] The concentrated soda lye may be treated until the initial concentration of 750 g./l. of NaOH is reduced to 450 g./l. The sodium carbonate monohydrate is only slightly soluble in the lye and is completely precipitated if the liquor is cooled to 25°C.;[3] alternatively further carbon dioxide may be added and the bicarbonate obtained.[2] The reduction in sodium chloride concentration due to electrolysis may be remedied by passing the electrolyte through a salt bed and carbonating it to precipitate bicarbonate.

Production of Sodium Carbonate from Sodium Bicarbonate.

Crude bicarbonate from the ammonia-soda process may be converted to sodium cyanide by reaction with carbon and nitrogen at high temperatures. The cyanide is eventually hydrolyzed to ammonia and sodium carbonate, some ammonia also being generated and recovered during the cyanidization.[85,86]

Production of Sodium Carbonate from Sodium Acetate.

Alkali-metal acetates are converted into the corresponding bicarbonates by the action of carbon dioxide on a concentrated aqueous solution in the presence of acetone at a temperature not exceeding 10°C. With sodium acetate it is preferable to have present a little potassium acetate. If the temperature is sufficiently low acetic anhydride is obtained, and may be recovered from its mix with the bicarbonates by centrifugal separation. The temperature may then be allowed to rise; the anhydride is converted into the acid and any residual bicarbonate into acetate.[87]

Production of Sodium Carbonate from Sodium Chloride.

Magnesium chloride and a suspension of pure lime in water give magnesium hydroxide; carbon dioxide converts this to magnesium carbonate, and further treatment with carbon dioxide and sodium chloride yields magnesium chloride and sodium bicarbonate.[89]

Sodium chloride may be added to a solution from urea synthesis containing urea and ammonia. Carbon dioxide is passed in, and sodium bicarbonate separated by filtration; the filtrate contains urea-ammonium chloride which can be used as a fertilizer. The sodium bicarbonate is washed with its 5% aqueous solution and heated to 120°C. to produce soda ash.[90]

Sodium chloride is decomposed by alumina at red heat to give $Al_2(ONa)_6$ and hydrogen chloride. The latter is used to attack dolomite giving magnesium and calcium chlorides, the liberated carbon dioxide being used to convert the aluminate to sodium carbonate and pure alumina.[91]

Production of Sodium Carbonate from Sodium Bisulphate.

Calcium cyanamide can be hydrolyzed to calcium hydroxide and bicyanamide, $Ca(HCN_2)_2$. Water and sodium bisulphate react with these to give calcium sulphate and sodium cyanamide, $NaHCN_2$. On heating the latter is converted according to the equation $2NaHCN_2 + 5H_2O \rightarrow Na_2CO_3 + 4NH_3 + CO_2$.[92]

Production of Sodium Carbonate from Sodium Sulphite.

The conversion is effected by treatment with ammonium bicarbonate, ammonium carbonate, or ammonia, carbon dioxide and water under atmospheric or greater pressure (55 lb./sq.in., 25–40°C.). A state of equilibrium is reached, but the formation of the carbonate or bicarbonate is favoured by passing the ammonium bicarbonate in countercurrent through the solid sodium sulphite. The ammonium sulphite left is contaminated with the other components in crystallization processes.[93]

Production of Sodium Carbonate from Sodium Nitrate.

Concentrated sodium nitrate solution is saturated with ammonia and carbon dioxide while the temperature is kept low. Sodium bicarbonate is filtered off and its equivalent in solid sodium nitrate is added and dissolved with agitation. On standing ammonium nitrate is precipitated.[96]

Sodium nitrate in liquid ammonia is carbonated to form sodium carbamate. The carbamate and water are led into a saturated aqueous solution of sodium carbonate monohydrate to effect hydrolysis of the carbamate when again the monohydrate is the only solid product.[97] Nitrates and phosphates in mixture may be treated to form bicarbonate, and ammonium phosphate and nitrate which are of use as a mixed fertilizer.[94,95]

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PHYSICAL PROPERTIES OF SODIUM CARBONATE AND SODIUM BICARBONATE

Sodium Bicarbonate

Sodium bicarbonate crystallizes in monoclinic prisms with 4 mols. per unit cell; $a = 7·51 \pm 0·04$, $b = 9·70 \pm 0·04$, $c = 3·53 \pm 0·03$ A., $\beta = 93°19'$. The calculated density is 2·16, observed 2·20–2·22. The space group is $P2_1/n$. The sodium atoms are surrounded by six oxygen atoms at 2·47 A.; the hydrogen and oxygen atoms form the OHO collinear group with O–H = 1·275 A. The plane of the optical axes is (010), the optical character is negative. The direction of the acute bisectrix is perpendicular to the (101) plane; the calculated and observed properties are respectively $\alpha = 1·393$, 1·380; $\beta = 1·480$, 1·500; $\gamma = 1·583$, 1·586; $2V = 92°$, 110°, where $2V$ is the true angle between the optic axes.[1,2] The molecular volume is 64·0 c.c.

The mean dielectric constant at 25°C. and low humidity at 10,000 c.p.s. is $\bar{\epsilon} = 4·39 \pm 0·04$ for the bulk crystals and $\epsilon_p \simeq 2·30$ for the bulk powder. The molecular polarizability, α_m, in cu. A. is 100·7 or 101·7 according as the bulk density value for the molecular volume, $V = 63·4$ c.c., or the X-ray value 64·0 c.c. is used.[3]

Anhydrous Sodium Carbonate, Na_2CO_3

The m.p. of the anhydrous salt is 856°C.[4] It crystallizes in flakes, biaxial, negative, $N_g = 1·544$, $N_m = 1·537$, $N_p = 1·410$. The two optic axes are inclined on the same side of the normal to the face of the flake, one very nearly coinciding with the normal; $2E = 43° \pm 2$, therefore $2V = 28° \pm 2$.[5] $2E$ being the apparent angle between the optic axes in air, $2V$ the true angle.

The density of anhydrous sodium carbonate varies greatly with its treatment and mode of formation, and may range from an apparent value of 0·38 to the true value 2·533 g./c.c.[6,7] The preparation of samples with densities appropriate to their commercial use is enlarged upon in the section on Utilization.

Crystallization is said to be promoted by passing an electric current through the solution.[8] Crystals of another habitus and larger than ordinary sodium carbonate may be got by adding small amounts of alginates to the saturated solution before cooling it below 31·4°C.; the crystals obtained are plates of 3–6 mm. with a thickness of 0·5 to 0·10 mm. They are larger than the ordinary crystals and less likely to be mistaken for common salt.[9]

The kinematic hardness is defined as the work necessary for compressing a unit volume of a solid with a given penetrator at a constant speed. The force is related to the penetration by the equation $F = kp^2$ in which K is a constant determined for each experimental curve and is 112 for sodium carbonate compared with 175 for steel, 74 for iron, 33 for sodium nitrate and 2·7 for lead.[10]

The magnetic susceptibility at 17°C. is $\chi = -0{\cdot}29 \times 10^{-6}$ c.g.s. e.m.u.[11–13]

The Hydrates and Molecular Compounds of Sodium Carbonate and Bicarbonate

Sodium Carbonate Monohydrate, Na_2CO_3,H_2O.

This may be prepared by evaporation of the saturated solution over sulphuric acid at 70°C. It is remarkably stable, absorbing no water when exposed for 30 min. to 80% relative humidity at 28°C.; only 0·14% increase occurs at 96% relative humidity. Samples exposed for several weeks to the atmosphere can be dried over calcium chloride in one hr.[14] It may be prepared in quantity by combining soda with an aqueous solution saturated with the monohydrate and maintaining the temperature within the stability limits (35–60°C.) of the monohydrate.[15]

It occurs naturally as thermonatrite in bipyramidal, rhombic crystals. It may be prepared commercially from sodium bicarbonate,[16] from $NaNH_4CO_3,2H_2O$,[17] from the decahydrate,[18] during the Solvay process,[19] or by adding soda ash heated to 120–150°C. to a saturated soda solution at 100°C., when granules of the monohydrate precipitate.[20]

The density of crystals grown from aqueous solution at 73°C. is 2·25 (International Critical Tables: 1·55). Data from oscillation photographs give a = 10·721 A., b = 6·440 A., c = 5·244 A., z = 4. The calculated density is 2·259.[21–23,7]

Sodium Carbonate Heptahydrate, $Na_2CO_3,7H_2O$.

The stable or α-form of this compound yields tabular crystals of orthorhombic symmetry with density 1·510 g./c.c.[7] The faces usually present are (010) (230)(100), the predominant terminal planes being (111) and (021). The crystals are flattened parallel to the brachypinacoid and the usual outline on the microscope stage shows a six-sided figure with angles of 128°40′ and 115°40′; or an eight-sided figure with 154°40′ and 115°40′; or still more rarely a rectangle. The extinction is parallel to (100) and bisects the 128°40′ angle. It readily loses water under atmospheric conditions and on heating gives a solution plus a new solid, the monohydrate.[24]

Sodium Carbonate Decahydrate, $Na_2CO_3,10H_2O$.

Monoclinic crystals with β = 122°42′. The most conspicuous terminal planes are (001), (10$\bar{1}$) and (111). If the crystals separate rapidly, columnar prisms terminated by the basal plane are obtained; if more slowly tabular forms flattened to (010) and terminated by (001) and (101) are formed. They form under the microscope an hexagonal figure with angles of 122°42′ (100):(001), 115°50′ (001):(101) and 121°68′ (101):(001). The birefringence is strong, extinction is parallel to (100). The three indices are 1·405, 1·425, 1·440.[7,24]

Examined on the stage of a heated microscope the decahydrate and the heptahydrate appear to melt incongruently at 32°C. and 35·5°C. respectively with congruent m.p.s at 34°C. and 45°C.[25]

The density is 1·460 g./c.c.[7,12] The mean value of the dielectric constant (powder) over the range 10–23°C. is 5·50.[26] The specific magnetic susceptibility, χ, at 17°C. is $-0{\cdot}56 \times 10^{-6}$ c.g.s. e.m.u.[12]

The solubility of the decahydrate is 49 g./100 g. H_2O at 11–12°C. At 25°C. it is 29·78 moles/1000 moles water.[24]

The efflorescence of the decahydrate is well known. The compound loses $8H_2O$ on drying in air for 45 days at ordinary temperatures; in 4 days over concentrated sulphuric acid it loses $8{\cdot}6H_2O$ and in 3 more days reverts to the monohydrate. In free-flowing cold air it is converted to the monohydrate in 14 hr.; 95% alcohol removes $4{\cdot}83H_2O$ in 24 hr. and $7{\cdot}4H_2O$ in 96 hr.; 79% removes only $2{\cdot}96H_2O$, and 60% none at all. The dehydration is complete in 3 hr. heating on a water-bath.[26-30] The compound can be dehydrated by passing into its aqueous solution the mixture of ammonia and water vapour obtained by distillation of the waste liquors of the Solvay process. As the ammonia concentration increases the anhydrous soda precipitates; the ammonia is a better dehydrating agent here than methyl or ethyl alcohol.[31]

The rate of absorption of moisture by the anhydrous salt at 18°C. has been determined for different degrees of humidity. Exposures up to 700 hr. were made: at the end of this period approximately 90% of the decahydrate water equivalent had been absorbed; for lower humidities (70%, 50%) the absorption was approximately 15 and 10% respectively.[32]

At 78% humidity soda ash is said to be less hygroscopic than potassium carbonate.[33]

Hydrates of Uncertain or Unconfirmed Composition.

Dihydrate, $Na_2CO_3,2H_2O$.

This has been reported as 'the stable final product' when the decahydrate is allowed to dry in air for 45 days; the monohydrate is said in the same investigation to revert to the dihydrate after standing in air for the same period.[29,30,34] Another worker confirms the dehydration to the dihydrate but describes it as irreversible, and finds that the anhydrous salt obtained by heating the dihydrate to 98°C. forms the stable monohydrate in air.[35] $Na_2CO_3,2H_2O$; $Na_2CO_3,4H_2O$ and $Na_2CO_3,6H_2O$ were all reported in an examination of the ternary system sodium carbonate–borax–water (see below).[36]

Hemipentahydrate, $2Na_2CO_3,5H_2O$.

The crystals are described as orthorhombic and biaxial negative, with $\alpha = 1{\cdot}435$, $\beta = 1{\cdot}492$, $\gamma = 1{\cdot}547$, $2V$ large; parallel extinction, negative elongation, $X = c$ and density $2{\cdot}053 \pm 0{\cdot}002$ (calculated from refractive index, 1·981).[7] They are stated also to appear in the reciprocal salt pair $2Na2K\|2ClCO_3$ (water), and indeed to be 'frequently separating', although no definite limits appear in the space diagram.[24]

Trihydrate, $Na_2CO_3,3H_2O$.

References to this compound occur occasionally and a transition to the monohydrate has been given as 39°C.[37]

$Na_2CO_3,4{\cdot}3H_2O$ has been reported.[11,12]

From a supersaturated solution of sodium carbonate a hydrate of unknown composition is said to crystallize, having a low positive temperature coefficient of solubility: it is 'easily converted into the hepta- or deca- hydrates'.[38]

Transition Phenomena in the Hydrates.

$Na_2CO_3,10H_2O \rightarrow Na_2CO_3,7H_2O$ 31·91°,[39] 31·85°,[40] 32·00°,[41] 32·02°C.[42]

$$(Na_2CO_3,10H_2O \rightarrow Na_2CO_3,H_2O\ 32{\cdot}96°C.)^{41}$$
$$Na_2CO_3,7H_2O \rightarrow Na_2CO_3,H_2O\ 35{\cdot}37^{41}$$
$$Na_2CO_3,H_2O \rightarrow Na_2CO_3\ 149°C.^{43}$$

The last transition temperature is lowered by adding readily soluble compounds, including those which form mixed crystals with soda. The hydrated forms generally may be converted into the anhydrous by heating at atmospheric pressure or below in suspension in the saturated solution above the transition temperature (with evaporation if required) in the presence of the addenda.[44] It is also lowered by increase of external pressure being 112·5°C. ± 1 at 1·27 atm.[5] The decahydrate and ice have a eutectic at –2·1°C. and 6·3 g. Na_2CO_3/100 g. H_2O; it was found that below 51 kg./cm.^{2} the effect of change of pressure is given by $dt/dp = -0{\cdot}0290$; above, to 926 kg./cm.^{2}, $dt/dp = -0{\cdot}0091$.[90] The air current method was used to explore the system $Na_2CO_3,10H_2O$–$Na_2CO_3,7H_2O$ between 0° and 50°C. The observed pressure, P, was at 0°C., 2·69 mm.; 15°C., 8·73 mm.; 25°C., 18·01 mm. At the transition temperature P(calc.) is 29·26 mm. The results can be represented by:

$$\log P = 11{\cdot}8071 - \frac{3634{\cdot}51}{T + 46{\cdot}45}.$$

Hence the heat of efflorescence per g. of water for the decahydrate is at 0°C.,. 676 g.-cal., 15°C., 686 g.-cal., 25°C., 693 g.-cal. The heat of reaction in kg.-cal. for $Na_2CO_3,7H_2O + 3H_2O$ is:[42]

Temp. °C.	0	15	25
Heat of reaction per mole of salt	4·36	5·32	5·98
Heat of reaction per mole of water	1·45	1·77	1·99

Binary Compounds excluding Water as a Component.
(See also below for the equilibria in the associated systems).

$Na_2CO_3,3NaHCO_3$, 'acid carbonate of sodium', can be produced by passing carbon dioxide saturated with moisture at 82°C. over pure dry soda at 95°C. with agitation,[45] or by heating a mixture of carbonate and bicarbonate of the requisite proportions to a temperature of about 95–100°C.[46]

$Na_2CO_3,4NaHCO_3$, recognized during a determination of the vapour pressures of water and carbon dioxide over heated bicarbonate, is also formed when sodium carbonate is kept in an equimolecular mixture of the two vapours.[47]

$Na_2CO_3,MgCO_3$ is hexagonal, sometimes rhombic.[48] It may be prepared by treating sodium chloride with magnesium carbonate in the presence of water saturated with carbon dioxide. The double salt is split by boiling.[49] It has been prepared from the solids by heating together at 1240 kg./sq.cm. pressure; m.p. = 677°C. under this pressure; a = 4·95, b = 8·52, c = 16·50 A.; n = 1·594 ± 0·003; density = 2·734.[57]

$Na_2CO_3,CaCO_3$ can be formed by the interaction of soda and calcium carbonate in the solid state[50] in an atmosphere of carbon dioxide. It has m.p. = 813°C.,[51] n = 1·547 ± 0·002, and a heat of formation of –2·02 kg.-cal./mole.[52,57]

$Na_2CO_3,2Na_2SO_4$ is *burkeite.*[52] It was first recognized as a new mineral species in the waters from Searles Lake where it was found at a depth of 115–130 ft.[53] The crystallographic constants have been determined and its occurrence as a solid phase in the system Na_2CO_3–Na_2SO_4–H_2O is described.

The crystals are orthorhombic with a rather large pinacoid face (100) and crystals lying on this face are most commonly observed microscopically. They are biaxial negative with $2V$ = 34° and the optic axial plane parallel to (100). The refractive indices are n_α = 1·451 ± ·003, n_β = 1·489 ± 0·003, n_γ = 1·491 ± 0·003, density = 2·57, hardness 3·5.[53,54]

$2NaHCO_3,MgCO_3$ is precipitated by treating a saturated solution of sodium chloride with more than 1 g.-mol. of magnesia or magnesium carbonate per litre under a carbon dioxide pressure of about 8 atm.[55]

$NaLiCO_3$. The compound has m.p. 514°C.;[56] a = 8·39, b = 14·22, c = 3·27 A.; *n* = 1·538 ± 0·003.[57]

Na_2CO_3,K_2CO_3. An early investigation indicated that $Na_2CO_3,K_2CO_3,12H_2O$ was the only compound involving the two salts.[58] The existence of the binary compound is said to be confirmed by the presence of an independent structure in the annealed and hardened mixtures, and by measurements of the refractive index.[59] In another examination the two carbonates were reported to form a continuous series of solid solutions.[60]

$Na_2CO_3,2CaCO_3$ is *shortite.*[214]

Ternary Compounds

Sodium Sesquicarbonate, $Na_2CO_3,NaHCO_3,2H_2O$.

This salt occurs naturally as *trona* and many patent specifications exist for its separation from this mineral and its preparation from its constituents. The crude trona may be dissolved in a brine of sodium carbonate and bicarbonate and passed to crystallizers where the sesquicarbonate is removed.[61-66] It may also be prepared indirectly during the Solvay process: thus ammoniacal aqueous sodium chloride may be carbonated below 40°C.,[67] or the bicarbonate treated with ammonia in the presence of aqueous sodium chloride to precipitate the sesquicarbonate.[68] It appears to be the major product of the evaporation of sodium bicarbonate solutions.

The crystallographic constants have been determined: the space group is C_{2h}^6, $a = 20{\cdot}41 \pm 0{\cdot}003$, $b = 3{\cdot}49 \pm 0{\cdot}01$ and $c = 10{\cdot}31 \pm 0{\cdot}01$ A. The carbonate ion is planar and regular with C–O = 1·23 ± 0·02 A., although one oxygen atom bonded to another by a hydrogen-bridge of 2·53 A. has C–O = 1·26 ± 0·02 A. forming what might be called a complex $[HC_2O_6]^{3-}$ anion. The water molecules are bonded by hydrogen-links of 2·72 ± 0·03 and 2·77 ± 0·03 A. to the oxygen atoms of the carbonate ions.[69]

$2(Na_2CO_3,NaHCO_3),H_2O$ is said to be produced when the bicarbonate is subjected to decomposition by heat in a saturated solution of common salt until carbonate and bicarbonate are present in equimolecular proportions; the material is cooled and the product removed.[44]

$Na_2CO_3,NaHCO_3,H_2O$ is the product if the decomposition is carried out until equimolecular quantities of carbonate and bicarbonate are present.[70]

$Na_2CO_3,NaHCO_3,4H_2O$ has been reported.[71]

$Na_2CO_3,K_2CO_3,12H_2O$. This compound has been readily separated and identified. Crystallographic examination shows the most strongly developed planes to be (110), (010), (100), (011), (101) and (111). Lying on the prismatic faces they give an extinction angle of 25°. The indices of refraction parallel and perpendicular to extinction are 1·428 and 1·440. When slowly heated it gives a clearly defined transition temperature of 34–35°C. but is readily reformed at temperatures as low as 0°C.[24,58] It was found in the reciprocal salt solution $2NaK||2ClCO_3(H_2O)$, probably contaminated by solid solution. The same author reports the compounds $Na_2CO_3,K_2CO_3,6H_2O$ and $Na_2CO_3,K_2CO_3,24H_2O$.[72]

$Na_2CO_3,CaCO_3,2H_2O$ is *pirsonnite*. Both this compound and *gaylussite* can be isolated as solid phases from aqueous solutions of sodium carbonate in contact with calcium carbonate, and in the sludge in the causticization process.[73]

$Na_2CO_3,CaCO_3,5H_2O$, *gaylussite.*[73] This compound may be formed in the soil: the condition for its stability is a soil solution of about 5% soda in contact with calcium carbonate; a soil in this state is completely sterile.[74] Gaylussite forms monoclinic crystals, transparent with a glass-like lustre: hardness is 2·5 and $d_4^{20} = 1{\cdot}991$. The crystals are completely fissile along the (110) plane. The optical orientation is $b = X$, $c\wedge Z = -14°$; the optical axial plane is perpendicular to the (010) plane. Indices of refraction for sodium light are α = 1·444, β = 1·516, γ = 1·523, all ± 0·001. 2V = 16°40′, 2E = 25°46′. Upon gradual heating to 100°C., the water is slowly given off.[209]

$Na_2CO_3,NaCl,MgCO_3$, *northupite* is regular octahedral, cubic. It can be prepared by mixing a solution of 1·5 g. of $MgCl_2$ in 5 ml. of water with another containing 15 g. of NaCl and 3·3 g. of Na_2CO_3 in 50 ml. of water, and agitating at 60°C. for 12 hr. It appears as a scale in the 'ammoniation' system in the Solvay process when untreated water is used.[48]

$K_2CO_3,NaHCO_3,2H_2O$ appears in the quaternary system.[75]

$2Na_2CO_3,KCl,9Na_2SO_4$ is *hanksite*. It occurs naturally.[210]

$2Na_2CO_3,2MgCO_3,Na_2SO_4$ is *tychite*.[213]

$Na_3Al(CO_3)_3,2Al(OH)_3$ is *dawsonite*.[213]

The Thermodynamic Properties of Sodium Carbonate and Bicarbonate.

The calculated values of the heat and free energy of formation and entropy change for the reaction $2Na(g) + C(graphite) + \frac{3}{2}O_2(g) \rightarrow Na_2CO_3(s)$ are compared with the observed values in Table V for T = 298°K.[76,77,79] Similar data are also given for the formation of the principal hydrates.

TABLE V.- THERMODYNAMIC DATA FOR SODIUM CARBONATE AND ITS HYDRATES

	ΔH_{298}(g.-cal.)	ΔG_{298}(g.-cal.)	ΔS_{298}(g.-cal./mole/deg.)
Na_2CO_3	−269,850	−249,960	32·7
	(−271,020)*	(−251,110)	(32·5)
Na_2CO_3,H_2O	−341,469	−307,493	-
	(−342,720)	(−308,640)	(40·7)
$Na_2CO_3,7H_2O$	−763,084	−648,894	-
	(−765,620)	(−647,890)	(94·5)
$Na_2CO_3,10H_2O$	−974,129	−819,456	-
	(−975,980)	(−818,430)	(128·2)

*Calculated values are in parentheses throughout.

The relative values of $H = H_T - H_{298}$ and of $S = S_T - S_{298}$ at higher temperatures are given in Table VI together with values of $\log_{10}K$ for the above reaction.[78]

TABLE VI.- THERMODYNAMIC DATA FOR Na_2CO_3 AT HIGHER TEMPERATURES

Temp.°K.	H	S	$\log_{10}K$
600	9,500	21·5	89·7
900	21,250	37·3	-
1,000	-	-	46·0
1,200	40,800	55·5	-
1,400	-	-	28·1

The molar heat capacities and entropies at 298°K. from calorimetric determinations are:-

	C_p(g.-cal.)	S
Na_2CO_3	26·41	32·5 ± 0·6
$NaHCO_3$	21·01	24·4 ± 0·4

The molar heat capacities between the experimental temperature limits (55 - 300°K.) are displayed in Fig. 6, the paper cited giving 13 determinations

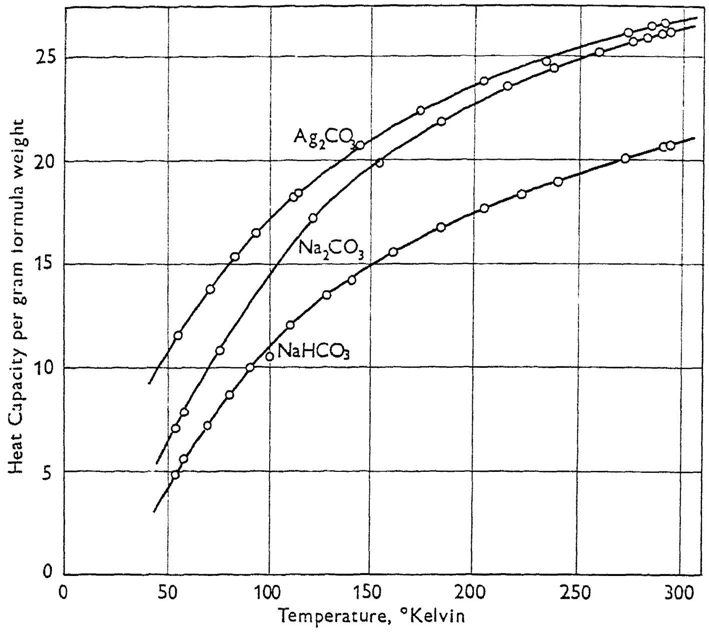

FIG. 6. THE HEAT CAPACITIES OF SODIUM AND SILVER CARBONATES AND SODIUM BICARBONATE, IN CALORIES PER GRAM FORMULA WEIGHTS

for Na_2CO_3 ranging from 6·877 at 54·60° K. to 26·29 at 292·1°K., and 17 for $NaHCO_3$ from 4·923 at 54·17°K. to 20·89 at 295·1°K. Two equations based on the Debye and Einstein functions have been fitted to the results.[77]

The molar heat capacity at high temperatures, determined by direct electrical heating for certain restricted ranges is given by the equation $C_p = A + (B \times 10^{-3})\theta$, where $A = 25{\cdot}06$, $B = 41{\cdot}84$ to ± 0·5% between 200° and 290°C., and $A = 30{\cdot}15$, $B = 19{\cdot}63$ to ± 0·5% between 500° and 600°C.[80]

Another source gives for the temperature range 300–500°K:-

$$C_{p(Na_2CO_3)} = 13{\cdot}98 + (5{\cdot}44 \times 10^{-2})T - (3{\cdot}125 \times 10^{-5})T^2$$

and

$$C_{p(NaHCO_3)} = 10{\cdot}97 + (3{\cdot}372 \times 10^{-2})T;$$

and for the reaction

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O\,(g)$$

$E_0^0 = 28{,}920$ g.-cal., $\Delta G^0_{298\cdot1} = 7083$ g.-cal. and $\Delta H^0_{298\cdot1} = 30{,}920$ g.-cal.[81]

The symbols have their customary significance[82,146] and for convenience are defined here: E_0^0 is the internal energy of the system in the ideal gas state at 0°K: superscripts refer to a property of the system in its standard reference state, generally the hypothetical gas state at a pressure of 1 atm. E is often written U.

H is the heat content of the system = $E + PV$; S = the entropy; G is the available energy (sometimes called the Gibbs free energy or the thermodynamic potential) = $E - TS + PV$.

E^0 is the total energy of the system = E_0^0 + energy due to all degrees of freedom.

$d(E^0-E_0^0)/dT$ is the specific heat.

The specific heat of anhydrous sodium carbonate at ordinary temperatures is 0·2728[83] or 0·2765,[84] the mean specific heat between 0° and 1500°C. being 0·433.[85] For the decahydrate, the specific heat is 0·415 and the molar heat capacity 118·9 g.-cal.[83]

The heat of fusion is given by $Na_2CO_3(s) \rightarrow Na_2CO_3(l)$; $\Delta H = 7000$ g.-cal.[86]

Polymorphic Modifications.

The heats of transition are $\alpha \rightarrow \beta$ Na_2CO_3, −200·6 ± 6·5 g.-cal./mole at 200–365°C., and β–γ Na_2CO_3, −448·5 ± 33·5 g.-cal./mole at 367–500°C.[80] The transition points have been determined as α–β 356°C., β–γ 486°C. and γ–δ 618°C. α and β are said to give a continuous series of solid solutions, whereas γ and δ show limited solubility.[59]

From specific heat anomalies and thermal expansion coefficients, a second-order transition (no latent heat, no change in modification) is believed to occur in anhydrous sodium carbonate at 360°C., and a first-order or 'announced' transition (polymorphic, 3% sudden increase in volume, with changes in conductivity and X-ray pattern, and a latent heat) at 481 ± 5°C.[87,123]

Heterogeneous Equilibria

The Behaviour of Systems Involving Sodium Carbonate or Bicarbonate as One Component.

Binary Systems.

(A) The second component is a liquid at ordinary temperatures.

(1) Sodium Carbonate–Water.

The hydrates of sodium carbonate have already been summarized. It has been pointed out that since the transition point in the system $Na_2CO_3,7H_2O$ Na_2CO_3,H_2O is 35·37°C. data for the solubility of sodium carbonate above that temperature at present recorded may refer to the composition of solutions in equilibrium with metastable monohydrate and require some revision.[37]

The solubility of sodium carbonate in water over the temperature interval 50–350°C.[5] is given in Table VII. and displayed in Fig. 7.

TABLE VII.- SOLUBILITY OF SODIUM CARBONATE IN WATER

Temp.°C.	%Na_2CO_3
50	32·0
100	30·8
112·5	30·8
121·5	29·8
131·5	28·8
159·0	26·8
180·0	25·0
239·0	18·7
300·0	8·4
321·0	4·8
326·0	4·4
348·0	0·0

A probable but undetectable solubility exists above 375°C., the critical temperature of water.

Concordant data for the intervals 16·6° to 173°C.[43] and 100°–200°C.[88] are

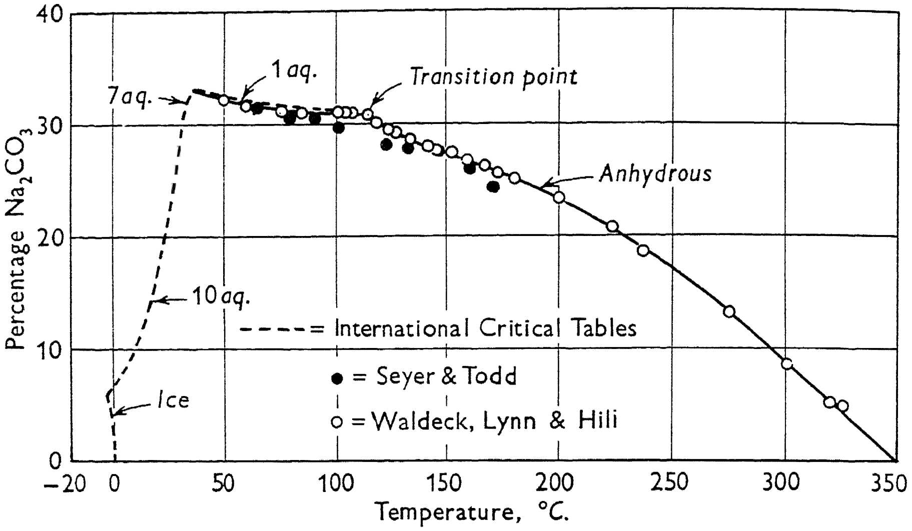

FIG. 7. THE SOLUBILITY CURVE OF SODIUM CARBONATE—'INTERNATIONAL CRITICAL TABLES' VALUES; ●SEYER AND TODD; o WALDECK, LYNN AND HILL

available; in the region 150°–350°C. later work suggests that at 350°C. the solubility is not negligible but is 2·0% Na_2CO_3.[54]

The solubility is markedly increased by the presence of nitrous gases, much higher concentrations being possible, a phenomenon of importance in the absorption of such gases commercially: the conversion of sodium nitrite to nitrate goes much better in concentrated solution.[89]

The corrected densities and viscosities (in poises) of aqueous solutions are listed in Table VIII.

TABLE VIII.- DENSITY AND VISCOSITY OF AQUEOUS SODIUM CARBONATE SOLUTIONS[91]

Temp.°C.	Normality of Na_2CO_3						
	0·000	1·000	2·000	3·000	4·000	5·000	6·000
	Density (g./c.c.)						
22·5	0·998	1·047	1·095	1·141	1·185	1·225	1·262
50	0·983	1·038	1·084	1·128	1·170	1·211	1·249
80	0·972	1·020	1·065	1·109	1·152	1·190	1·228
98	(0·960	1·009	1·054	1·098	1·140	1·177	1·214)
						by extrapolation	
	Viscosity (poises)						
22·5	0·00949	0·01201	0·01564	0·02116	0·02863	0·03980	0·05650
50·0	0·00549	0·00756	0·00976	0·01283	0·01678	0·02246	0·02994
98·0	0·00289	0·00347	0·00428	0·00530	0·00647	0·00794	0·00960

The data in Table IX are applicable between 9°C. and 30°C. and give the viscosity η in terms of the coefficients in the expression $\eta = k - k't + k''t^2$.

TABLE IX.- VISCOSITY COEFFICIENTS IN POISES FOR AQUEOUS SODIUM CARBONATE SOLUTIONS[92]

Concn. in g.-moles		k	k'	k''
Na_2CO_3	H_2O			
1	52	0·0310	0·00088	0·000010
1	100	0·0223	0·000576	0·0000060
1	200	0·01958	0·000521	0·00000576

The specific viscosity (viscosity of solution/viscosity of water at the same temperature) is given in Table X.

TABLE X.- THE SPECIFIC VISCOSITY OF AQUEOUS SODIUM CARBONATE SOLUTIONS

Moles/1000 g. water	Viscosity at:		
	20°	30°	40°
0·1	1·049	1·053	1·051
0·25	1·128	1·137	1·133
0·5	1·279	1·293	1·285
1·0	1·673	1·688	1·649
2·0	3·125	2·970	2·830

In the same paper are recorded the absolute viscosities and the solution densities over a wide range of concentrations (from 1 N. to supersaturation). The selected data in Table XI supplement those in Table VIII.

TABLE XI.- VISCOSITY IN POISES FOR CONCENTRATED AQUEOUS SODIUM CARBONATE SOLUTIONS

G. equiv. Na_2CO_3	20° C.	d corrected to vacuo	Viscosity
4·824	super-saturated	1·2240	0·043515
5·684		1·2591	0·060158
6·620		1·2946	0·08695
7·618		1·3308	0·13228
	40° C.		
4·786		1·2137	0·024248
5·639		1·2483	0·031583
6·570		1·2838	0·041840
7·533		1·3199	0·057324

Data are given in addition for 30°C.; and for mixtures with 25·3, 49·5 and 73·5% NaOH.[93]

At 25°C. the density of aqueous sodium carbonate solutions is said to vary linearly with concentrations from 1 to 12%.[100] The viscosity is constantly higher than with potassium carbonate.

The molecular volume at 25·00°C. is a linear function of the square root of the concentration for solutions greater than 4·8 N.[94] The apparent molal volumes of sodium carbonate in sodium chloride solutions have been determined at 25°C. up to a volume ionic strength of unity; they increase from negative to positive with an increase in volume ionic strength.[95]

Another investigator has examined the dependence on concentration of the apparent molecular volume and refraction in dilute solutions (0·01 to 1·5 N.)[96] In the same paper the percentage hydrolysis, h, has been calculated from the activity coefficient, γ, for moderate concentrations and compared with earlier work[97] as in Table XII.

TABLE XII.- ACTIVITY COEFFICIENTS AND DEGREES OF HYDROLYSIS IN AQUEOUS SODIUM CARBONATE SOLUTIONS (AT 25°C.)

C_v (equiv./l.)	$f = \frac{\gamma_{HCO_3^-}\,\gamma_{OH^-}}{\gamma_{CO_3^=}}$	h%	Ref.
0·00076	1·077	63	97
0·00095	1·085	55	97
0·001900	1·123	36	97
0·003780	1·175	23·6	97
0·004714	1·197	20·6	97
0·009294	1·30	13·7	97
0·0232	1·23	11·9	96
0·0287	1·26	10·0	96
0·1094	1·57	4·6	96
0·1591	1·73	3·6	96
0·415	2·43	1·9	96

The densities and volume changes (Δv) on solution in ml./g.-equiv. at 20°C. for very dilute solutions are given in Table XIII.

TABLE XIII.- DENSITIES AND VOLUME CHANGES IN DILUTE SODIUM CARBONATE SOLUTIONS[97]

C_v	d_{20}^{20}	Δv
0·0001	$1{\cdot}0000056_8$	$-24{\cdot}5_6$
0·0002	$1{\cdot}0000112_5$	$-24{\cdot}5_7$
0·0004	$1{\cdot}0000225_1$	$-24{\cdot}5_8$
0·0005	$1{\cdot}0000281_4$	$-24{\cdot}5_9$
0·0010	$1{\cdot}0000563_2$	$-24{\cdot}6_2$
0·0020	$1{\cdot}0001127_5$	$-24{\cdot}68_2$
0·0040	$1{\cdot}0002258_5$	$-24{\cdot}76_8$
0·0050	$1{\cdot}0002824_5$	$-24{\cdot}79_6$
0·0100	$1{\cdot}0005648_0$	$-24{\cdot}78_6$

The densities and molar contractions for temperatures up to 60°C. and 1 to 30% Na_2CO_3 have been reported.[101] Typical data are:

	d_{20}	Mol. vol.(c.c.)	
$Na_2CO_3, 10H_2O$	1·450	197·2	Molecular contraction in c.c. in the solid hydrated crystal is 25·2
Na_2CO_3	2·500	42·4	

There is no indication in the molar contractions of transition points corresponding to the dissociation of definite hydrates.[102] A nomographic chart giving temperature correction scales for the densities of soda ash solutions is available: two sections are necessary since solutions of density greater than 1·1150 become supersaturated above 15°C. Densities in degrees Beaumé and the percentage composition as sodium carbonate or decahydrate are recorded.[103]

The adiabatic compressibilities of various aqueous solutions of sodium carbonate have been determined by means of an ultrasonic interferometer over a range of temperatures.[104] In one investigation they were shown to fit the equation:

$$\beta = \beta_1 + A'C + B'C^{3/2}$$

where β is the compressibility of the solution, β_1 that of the pure solvent and

C the molar concentration. Data are available for 10^{-4} M. to 1·0 M. For Na_2CO_3 if $\phi(\bar{K}_2)$ is the molar compressibility, $\partial\phi(\bar{K}_2)/\partial\sqrt{c}$ at 25°C. is 48·8 × 10^{-10} [98,99]

Direct measurements of the compressibility from 1 to 1000 bars for the entire solubility range have been made; an equation expressing the apparent compression of the salt as a linear function of the square root of the volume concentration is the most useful way of representing the results.[106]

The equivalent refraction at 25°C. from N. to saturation is a rising linear function of the concentration. (See Table XIV.)[108]

TABLE XIV.- EQUIVALENT REFRACTIONS OF SODIUM CARBONATE SOLUTIONS

Normality of solution	d_4^{25}	$n_{D_3}^{25}$	R_{D_3}
0·0	0·99707	1·33257	(6·27$_0$)
0·9518	1·04671	1·34300	6·283
1·3298	1·06535	1·34679	6·290
1·8494	1·09000	1·35170	6·296
2·6585	1·12690	1·35887	6·303
3·6322	1·16887	1·36683	6·314
4·9102	1·22260	1·37657	6·322

$\Delta R/\Delta C_g = +\ 0{\cdot}012$ where $\Delta R = R_C - R_O$ in 10^{-2}cm.^{3}. By extrapolation to zero concentration the sum of the refraction of the dissolved ions is 6·27$_0$ the equivalent refraction of Na^+ being 0·200, $\frac{1}{2}CO_3''$ = 6·07$_0$.

Sound absorption measurements have been made for aqueous sodium carbonate up to 300 Mc./sec.[109] To a first approximation the dependence of the attenuation on concentration is linear.[107] Measurements have also been made of the change in the velocity of sound in water while the salt is dissolving.[110]

The maximum concentrations of supersaturated solutions of the anhydrous and hydrated salts are said to obey Le Chatelier's solubility law, and they should be considered as the 'second' solubility of a given substance. Data are available for the three hydrates of sodium carbonate.[111]

Solubility in Non-aqueous Solvents.

Sodium carbonate is markedly insoluble in solvents other than water. Few measurements have been made.

The solubility in ethyl alcohol is 0·0088 g. of anhydrous salt per 100 ml., at 25°C.[112] (Potassium carbonate gives 0·1114 g./100 ml.). The solubility in liquid ammonia at 25°C. is negligible.[113]

Heats of Solution and Dilution.

It may be convenient to summarize the conventional special cases for heats of solution:[82] the initial heat of solution L_0 is the heat absorbed when 1 mole of solute A dissolves in a very large amount of solvent B; the final heat of solution L_S absorbed when 1 mole of A dissolves in a large mass of practically saturated solution of concentration $c = s$; the integral heat of solution L_C absorbed when 1 mole of A dissolves in so much solvent as produces a solution of concentration c; the differential heat of solution L_C absorbed when 1 mole of A dissolves in a large mass of solution of concentration c; the integral heat of dilution D_c absorbed when a solution containing 1 mole of A at concentration c is mixed with a large mass of solvent; the differential heat of dilution $\bar{D}_c$ absorbed when 1 mole of solvent B is added to a very large mass of solution of concentration c.

In the reaction $Na_2CO_3(s) + H_2O(1000\ \text{moles}) \rightarrow Na_2CO_3\,aq.$, at 25°C. $\Delta H = -L_c = -5606{\cdot}7 \pm 22{\cdot}1$ g.-cal.[114,115] At 30°C., to form a solution containing 5·13% by weight, the heat of solution is 6·49 ± 0·02 kg.-cal./mole.[116]

The heat of dilution of a 28·24% solution at 30°C. is $D = -2{\cdot}066Y/(Y + 54{\cdot}8)$g.-cal. per mole Na_2CO_3 where Y is the number of moles of water used in diluting the solution.[116]

A number of empirical equations for the heat of dilution in special cases are available:[117] thus for $n = 15$ moles water/s moles of salt at 18°C.

$$[D^{18}]_n^{200} = (-106709 + 533{\cdot}5n)/(n + 24{\cdot}8)$$

and

$$[D^{18}]_{200}^{\infty} = -533{\cdot}5 \text{ g.-cal.}$$

and for infinite dilution

$$D_c \text{ for } Na_2CO_3,nH_2O \rightarrow \infty H_2O = -\frac{119940}{n + 24{\cdot}8}$$

An exhaustive investigation provides data and numerous graphs for the various heats of solution and dilution of Na_2CO_3 and $Na_2CO_3,10H_2O$.[83] Figs. 8 and 9 are typical

The heat capacity in g.-cal./g. for aqueous sodium carbonate is given in Table XV.

TABLE XV.- HEAT CAPACITY OF AQUEOUS SODIUM CARBONATE SOLUTIONS[116]

Temp. 17·6°C.		Temp. 30°C.		Temp. 76·6°C.		Temp. 98·0°C.	
Concn. c, in wt.-%	c_p	c	c_p	c	c_p	c	c_p
0·000	0·9992	0·000	0·9986	0·000	1·0098	0·000	1·0084
1·498	0·9807	2·000	0·9786				
2·901	0·9597	4·000	0·9594	5·000	0·9761		
5·000	0·9428	6·000	0·9392				
8·000	0·9183			10·00	0·9452		
10·00	0·9086						
13·79	0·8924	13·84	0·8881				
		20·00	0·8631	20·00	0·8936		
				25·00	0·8615	25·00	0·8911

$Na_2CO_3,10H_2O$.

The final heat of solution, the integral heat, and the initial heat of dilution are respectively $L_S = -12{,}642$ g.-cal., $L_c = -27{,}981$ g.-cal., and $D_0 = -1503$ g.-cal.[79]

The initial heat of solution L_c is given by

$$Na_2CO_3,10H_2O(s) + H_2O(1000\text{moles}) \rightarrow Na_2CO_3\,aq; \quad \Delta H = 16{,}370 \text{ g.-cal.}^{83}$$
$$(\Delta H = -L_c)$$

Enthalpy (heat-content) diagrams have been constructed for binary aqueous mixtures at fixed pressures for sodium carbonate and hydrazine and glycerol. The steps in the production of such diagrams are outlined.[211]

The solubility equation of a salt hydrate S,sH_2O can be written

$$503\,\frac{C}{1-sC}\,\frac{L_S}{T^2} - (\partial \log p/\partial C)_T\frac{dC}{dT} = 0$$

where T = absolute temperature, C = moles of salt in the saturated solution per mole total water; L_S = final heat of solution of the hydrate and p = vapour pressure of solution near saturation. For $Na_2CO_3,10H_2O$, $C_{20} = 0{\cdot}0365$, $dC/dT = 0{\cdot}00213$.

The vapour pressures of solutions of sodium carbonate decahydrate at

20°C. are given in Table XVI.

TABLE XVI.- VAPOUR PRESSURES OF SODIUM CARBONATE DECAHYDRATE SOLUTIONS AT 20°C.

Concn.	p (mm. Hg)
0·00641	17·30
0·0123	17·10
0·0197	16·78
0·0256	16·60
0·0305	16·41
0·0312	16·37
0·0334	16·31
0·0365	16·20
(sat.)	(extrap.)

The above results give $L_S(20^\circ) = -13{\cdot}96$ g.-cal. and $(\partial \log p/\partial C)_{20^\circ} = -2{\cdot}18$ where L_S(calc.) = $-13{\cdot}78$ g.-cal.[118] The extrapolated value obtained by adding increasing amounts of salt to the solution is $-13{\cdot}54$ g.-cal.

Vapour Pressures of Sodium Carbonate Hydrates and Solutions.

Vapour pressures of sodium carbonate solutions are recorded in Tables XVII and XVIII.

TABLE XVII.- VAPOUR PRESSURES OF SODIUM CARBONATE SOLUTIONS[121]

Molality (moles/1000 g. solvent)	V.p. in mm.		
	t = 65°C.	t = 80°C.	t = 95°C.
0·1009	187·6	353·5	631·4
0·1999	185·9	351·9	628·7
0·5914	182·9	346·6	619·0
1·0001	180·2	342·1	610·2
2·520	169·8	324·1	578·2

TABLE XVIII.- VAPOUR PRESSURES OF SATURATED SODIUM CARBONATE SOLUTIONS[5,212]

Temp.°C.	V.p. in atm.
104·8	1·00
112·0	1·27
121·0	1·69
176·5	8·43
231·0	26·6
313·0	99·0
365	199

Dissociation pressures for the system: $Na_2CO_3,7H_2O \rightarrow Na_2CO_3,H_2O + 6H_2O$ are given by $\log P(\text{mm.}) = 10{\cdot}2960 - (2704{\cdot}9/T)$.[79]

Activity Coefficients in Sodium Carbonate Solutions.

For aqueous sodium carbonate these are very closely represented by the Debye–Hückel relation:

$$\log \gamma_\pm = \frac{-S_f\sqrt{\Gamma}}{1+A\sqrt{\Gamma}} + Bc - \log(1 + 0{\cdot}054m),$$

where $\gamma_\pm$ = mean ionic molal activity coefficient; S_f = limiting slope of the Debye–Hückel curve; Γ = initial concentration; A,B are constants; c = molarity in moles/1000 ml. of solution; m = molality in moles/1000 g. of solvent.[121] Corresponding data are listed in Table XIX.

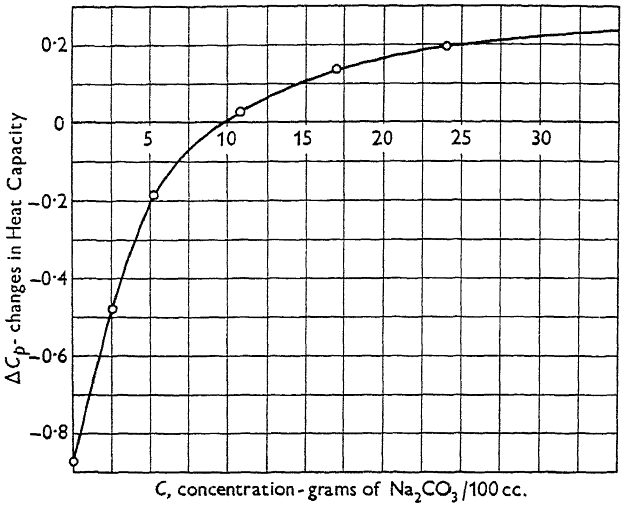

FIG. 8. CHANGES IN HEAT CAPACITY ON DISSOLVING 10g. OF Na_2CO_3 IN AN INFINITE AMOUNT OF SOLUTION OF CONCENTRATION *c*

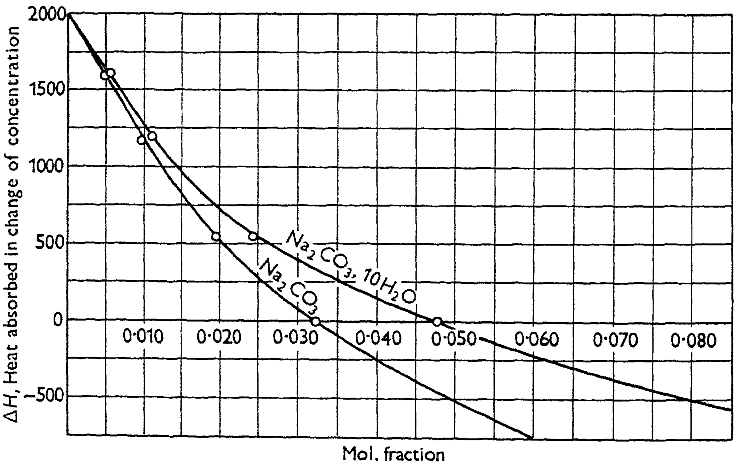

FIG. 9. HEAT ABSORBED IN DILUTION OF SOLUTIONS CONTAINING ONE MOL. OF Na_2CO_3 OR $Na_2CO_3, 10H_2O$

The results accord well with those determined from vapour pressure measurements and given in Table XX.

TABLE XIX.- ACTIVITY COEFFICIENTS IN SODIUM CARBONATE SOLUTIONS

Molality	$\gamma_\pm$				
	15°C.	25°C.	37·5°C.	50°C.	65°C.
0·2008	0·371	0·393	0·441	0·406	0·471
0·6012	0·273	0·300	0·349	0·367	0·365
1·5355	0·210	0·230	0·268	0·274	0·263

TABLE XX.- THE ACTIVITY COEFFICIENTS IN SODIUM CARBONATE SOLUTIONS FROM VAPOUR PRESSURE DETERMINATIONS

Molality	$\gamma_\pm$		
	65°C.	80°C.	95°C.
0·2000	0·462	0·423	0·382
0·5000	0·379	0·330	0·300
1·000	0·308	0·254	0·240
2·000	0·250	0·193	0·184
2·500	0·237	0·183	0·173

The same investigation provides tables of the relative partial molal enthalpies (heat contents) at different temperatures and a number of curves relating to activity coefficient data.

Interfacial Tensions of Aqueous Solutions.

The surface tension and viscosity of aqueous sodium carbonate have been determined at 20°C. by the drop-weight method.[124] They are given in Table XXI.

TABLE XXI.- SURFACE TENSION AND VISCOSITY OF SODIUM CARBONATE SOLUTIONS

Normality	Wt.-% Na_2CO_3	d, g./c.c.	Surface tension dynes/cm.	Viscosity (c.g.s. units)
1·03	5·22	1·055	73·7	0·0114
2·22	10·60	1·111	74·9	0·0144
3·935	17·54	1·1891	77·3	0·0221

The interfacial tension between aqueous solutions of sodium carbonate (0·001 to 0·1 M.) and certain asphalts has been determined and shown to be inversely proportional to pH of the solutions and to their concentration.[125]

The heat transmission coefficient $Z = K(\rho C_p)^m/\lambda^{m-1}$ for sodium carbonate solution (200g./l.) is 1785 compared with 1760 for pure water. The quantities on the right-hand side of the equation are given in the original paper in curves as a function of the temperature.[126]

(2) Sodium Bicarbonate-Water.

The solubility of the bicarbonate in water is as follows:[127-129]

Temp.°C.	Solubility (g./100g.water)
20	9·55
25	10·31
30	11·05
40	12·57

Values for elevated temperatures under the natural pressure of the system are:[128]

Temp. °C.	Solubility (wt.-% Na_2CO_3)
100	19·1 ± 0·2
150	27·2 ± 0·7
170	32·0 ± 1·0
190	37·5 ± 1·0
200	43·0 ± 1·0

The solubility defined as $L = [Na^+][H_3CO_3^-]$ is given by $\log L = -679/T + 4{\cdot}87$.[130]

The solution of 1 mole in 400 moles of water gives for the initial heat L_O −4·58 kg.-cal. and for the final heat, L_S, −3·92 kg.-cal.[131]

The contraction on solution in water has been examined and shown to increase with concentration.[132]

On dialysis the CO_2/Na value of a bicarbonate solution is reported as varying from 1·98 to 1·74 during a period of 2 hr.[133]

In aqueous solution sodium bicarbonate very slowly decomposes at ordinary temperatures; in the course of several weeks carbonate is formed in closed containers, but more quickly in open vessels: brief treatment with hot water causes only a slight change, but persistent boiling produces increasing change, the decomposition velocity however gradually diminishing as carbonate accumulates, 95% being transformed in 5 hr. boiling.[134]

The formula of Gmelin–Kraut[135] has been checked with experimental results with fair success. At 25°C. the theoretical and experimental values for the percentage decomposition of $NaHCO_3$ in aqueous solution are respectively:[136]

	1·0 N.	0·3 N.	0·1 N.
Th.	11·4%	23·0%	39·0%
Exptl.	12·5%	23·2%	40·7%

The equilibrium in the system CO_2–Na_2CO_3–$NaHCO_3$–H_2O has been quantitatively examined. Values for the McCoy coefficient $M = 2X^2C/SP(1 - X)$ were determined, and a new equation derived suitable for any sodium-ion concentration between 0·5 and 2 N. and for any temperature from 20° to 70°C.; it is $X^2C^{1{\cdot}29}/SP(1 - X)(185 - t) = 10$ where X = fraction of carbonate converted to bicarbonate, $C = [Na]$, S = solubility of carbon dioxide at the temperature t, and P is the pressure in atm.[137]

The decomposition by hydrolysis of aqueous sodium carbonate between 147° and 243°C. appears to produce sodium bicarbonate as well as hydroxide, especially in high-pressure steam boilers.[138]

In boiling aqueous sodium bicarbonate, the value of the ratio of decomposed to residual bicarbonate falls with increasing concentration. The effect is attributed to H^+ and OH^- present.[139]

(B) The second component is a solid.

(3) Na_2CO_3-$CaCO_3$.

Fused mixtures of calcite and soda behave in relation to their thermal dissociation as ideal solutions of the double salt $CaCO_3,Na_2CO_3$ in sodium carbonate. The two constituents are miscible in all proportions and the dissociation pressure is a linear function of the molecular concentration.[140] It is found that sodium carbonate promotes the dissociation of calcium and magnesium carbonates.[141] The two salts are also said to form solid solutions with maximum melting point 875°C. at 7 equiv.-% $CaCO_3$, and a eutectic at 786°C. with 38 equiv.-% $CaCO_3$.[51] Solid phases here are a solid solution and the binary compound $CaCO_3,Na_2CO_3$ which has a melting point 813°C.

(4) Na_2CO_3–NaCl.
A eutectic with 46·5 mol.-% Na_2CO_3 at 645°C.[4] On dynamic heating endothermic effects are observed at 638° and 840°C.[143]

(5) Na_2CO_3–NaBr.[60,142]
A eutectic system.

(6) Na_2CO_3–NaI.[60]
A eutectic system.

(7) Na_2CO_3–$BaSO_4$.[144]

(8) Na_2CO_3–Na_2CrO_4.[51]

(9) Na_2CO_3–KCl.
A eutectic with 42·5 mol.-% Na_2CO_3 at 587°C.[4]

(10) Na_2CO_3–Li_2CO_3.
Two eutectics at 39% and 44% Li_2CO_3. Compound $NaLiCO_3$, m.p. 514°C.[56]

(11) Na_2CO_3–K_2CO_3.
Uninterrupted solid solutions with a minimum melting point at 40 mol.-% K_2CO_3 and 706°C.[59]

(12) Na_2CO_3–NaOH.
Data are given for this system up to 35% carbonate.[86] A transition point (NaOH) occurs at 294°C. and a eutectic at 286°C. (Fig. 11).

(13) $Na_2CO_3,10H_2O$–$Na_2S_2O_3,5H_2O$.
The system has one eutectic and no compounds.[145]

(14) Na_2CO –$BaTiO_3$.
Eutectic at 1·4% Na_2CO_3, m.p. 826°C.[147]

(15) Na_2CO_3–$PbTiO_3$.
A eutectic at 0·15 mole% Na_2CO_3 and 830°C.[148]

(16) Na_2CO_3–NaCN.
The mixture behaves ideally with respect to the total vapour pressure in the neighbourhood of 1000°C.; it is a linear function of the composition.[150]

(17) $MgCO_3$–$NaHCO_3$.
The heating curves have been studied,[149] indicating the feasibility of determining the heats of dehydration and dissociation.

Ternary Systems.
The following summary includes the more important investigations, especially where the isotherms are available and the data reasonably complete. Points of interest are mentioned.

(A) One component is water.

Na_2CO_3–Li_2CO_3–H_2O. 25°C.
No equilibrium diagrams but tabulated results. No compounds were isolated.[151]

Na_2CO_3–K_2CO_3–H_2O.
–37° to 25°, 80° to 150°,[152] –30° to 12·6°,[153] 80°, 100°, 125°, 150°,[88,154] 100°, 150°,[155] 100°, 120°, 140°, 145°,[156] 100°, 150°,[157] 20°, 25°, 30°, 33°, 36° and 50°,[158] –6°, 10°, 24·2° and 40°C.[92]

The equilibria are of course of importance in the separation of naturally occurring mixtures of sodium and potassium salts.

Some lack of agreement is shown. At 20–34°C. in contact with liquid

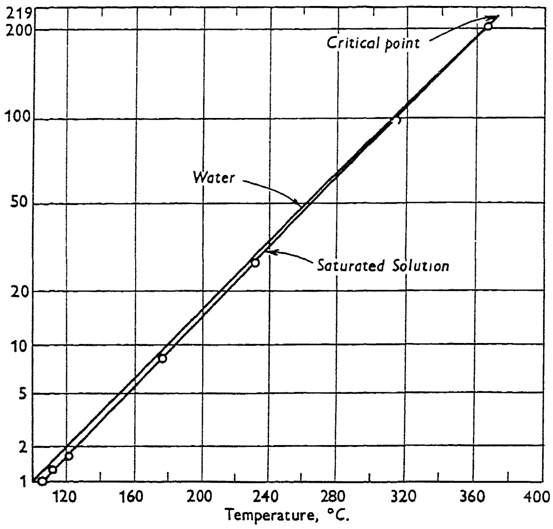

FIG. 10. THE VAPOUR PRESSURE OF SATURATED SOLUTIONS OF SODIUM CARBONATE PLOTTED BY DÜHRING'S METHOD

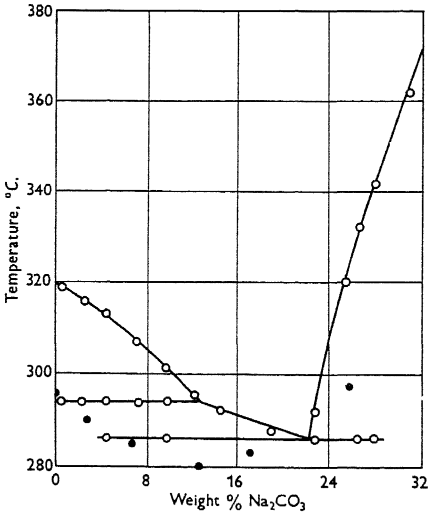

FIG. 11. TEMPERATURE-COMPOSITION DIAGRAM FOR THE SYSTEM Na_2CO_3-NaOH: o SEWARD: ●NEUMAN AND BERGVE

solutions of certain concentrations a series of ternary solid solutions of formula $(K_2,Na_2)CO_3,6H_2O$ is obtained in which the atomic ratio K/Na varies from 1:0·88 to 1:2·07.[158] Figs. 12–16 show the conditions between 25° and 36°C.[158] From 25·12°C. upwards in contact with solutions rather high in potassium carbonate K_2CO_3,Na_2CO_3, is stable over increasing ranges with in-

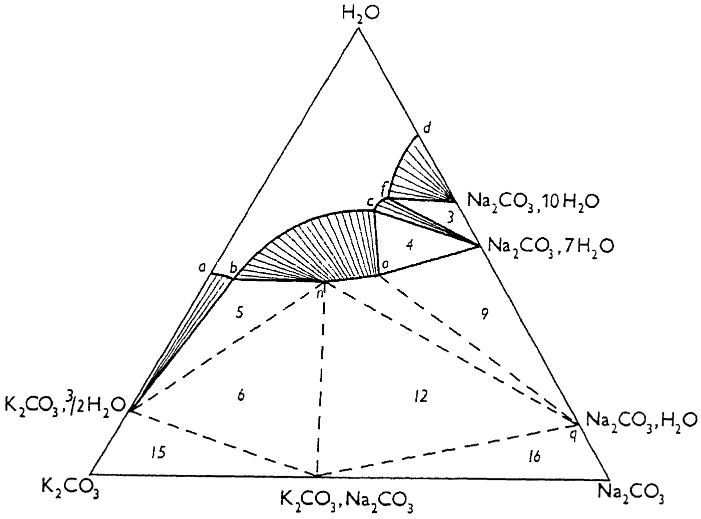

FIG. 12. 25°C. ISOTHERM FOR Na_2CO_3-K_2CO_3-H_2O

creasing temperature and is confirmed up to 450°C. An interesting confirmation of van't Hoff's law of mobile equilibrium: the water of crystallization of the two constituents is greater than that of the double salt, which is thus produced from the former on raising the temperature. It is incongruently soluble from 100° to 150°C. and decomposes to give Na_2CO_3,H_2O or Na_2CO_3 and a solution.[155] Another investigation indicated that the double salt field became smaller with rise in temperature, and disappeared at 140°C., an industrial process being based on this.[156,157]

A consolute temperature exists between 20 and 50°C. in which two liquid solutions become identical, and again with two solid solutions (Figs. 12–16). The solubility of potassium carbonate is much lower in saturated aqueous sodium carbonate.[159]

Na_2CO_3-$CaCO_3$-H_2O.

The concentration of calcium carbonate in the solution is too small to measure. The solid phases present at various temperatures are ice, $CaCO_3$, $Na_2CO_3,10H_2O$, $Na_2CO_3,7H_2O$, Na_2CO_3,H_2O, $Na_2CO_3,CaCO_3,5H_2O$ (gaylussite) and $Na_2CO_3,CaCO_3,2H_2O$ (pirssonite).[73]

Na_2CO_3-$Na_2B_4O_7$-H_2O. 30°, 35°, 50°, 55°, 60°C.

$Na_2CO_3,2H_2O$, $Na_2CO_3,4H_2O$ and $Na_2CO_3,6H_2O$ are said to be formed, and $Na_2B_4O_7,H_2O$ at 55°C.;[36] beyond 35°C. the system is said to become quaternary owing to the formation of sesquicarbonate, $Na_2CO_3,NaHCO_3,2H_2O$.[160]

Na_2CO_3-$NaNO_2$-H_2O. 10–30°C.

Sodium carbonate exercises a salting-out influence on saturated sodium nitrite solutions.[161]

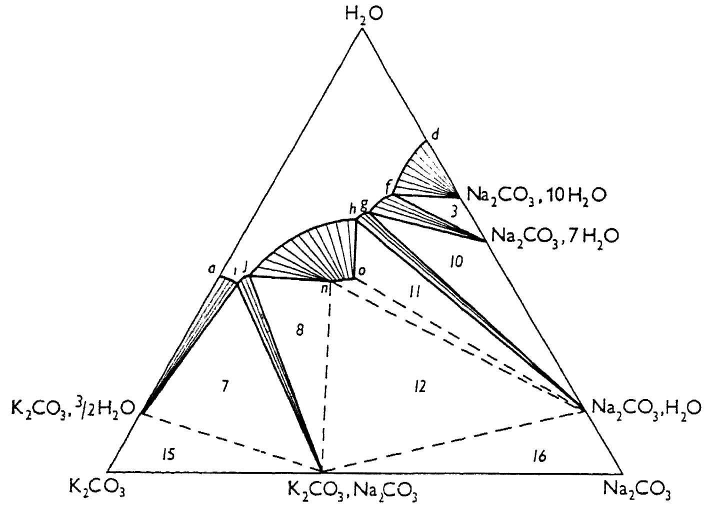
H_2O
d
$Na_2CO_3,10H_2O$
f
3
$Na_2CO_3,7H_2O$
h
g
10
a
i
j
o
n
11
8
7
12
$K_2CO_3,{}^3/_2H_2O$
Na_2CO_3,H_2O
15
16
K_2CO_3
K_2CO_3,Na_2CO_3
Na_2CO_3

FIG. 13. ISOTHERM ABOVE 26·76°C. FOR Na_2CO_3-K_2CO_3-H_2O

Na_2CO_3-Na_3PO_4-H_2O. 25°C.

$Na_2PO_4,12H_2O$ and $Na_2CO_3,10H_2O$ occur, but no double salts. The 'eutonic' mixture contains Na_3PO_4 6·40, Na_2CO_3 10·30, H_2O 74·30 wt.-%.[162]

Na_2CO_3-Na_2S-H_2O. 30°C.

Equilibrium reached in 4 hr. The solubility of sodium carbonate decreases markedly with increase in sulphide concentration and with rise of temperature in saturated sulphide solution, 10·16 wt.-% at 30°C., 6·7% at 60°C. and 4·46% at 80°C.[163]

Na_2CO_3-$NaCl$-H_2O. −21·4° to 60°C.

Equilibrium diagrams are available.[164]

Na_2CO_3-$NaOH$-H_2O.

The reciprocal solubilities have been determined at 150°, 250° and 350°C.

	Solubility, g./100 g. H_2O	
	NaOH	Na_2CO_3
150°C.	7·2	26·2
	19·5	13·4
250°C.	8·1	14·2
	21·4	11·5
350°C.	8·1	4·9
	20·2	12·7

Sodium hydroxide depresses the concentration of sodium carbonate at 150° and 250°C. with respect to all solid phases, but at 350°C. the carbonate

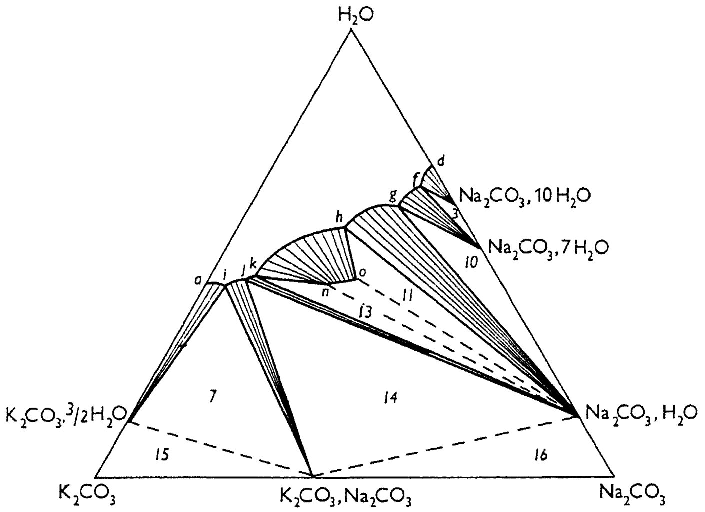

FIG. 14. 30°C. ISOTHERM FOR Na_2CO_3-K_2CO_3-H_2O

concentration greatly increases with addition of caustic soda. (Fig. 17.)[54] Three Russian sets of data are available, the first of which differs markedly from the others and from this work.[52,165,166]

At 100°C. a transition point occurs at 13·4% NaOH with Na_2CO_3 and Na_2CO_3,H_2O in stable equilibrium. At higher NaOH concentration the stable phase is Na_2CO_3, but is monohydrate in the lower concentration range. The solubility of sodium carbonate at this temperature is some 93 times greater in water than in 48% caustic soda.[52]

Na_2CO_3-$NaClO_3$-H_2O.

See below: 'Reciprocal Salt Pairs'.[72]

Na_2CO_3-$KClO_3$-H_2O.

The solubility of the chlorate in g./100ml. of 5% or 7% aqueous sodium carbonate is:-

Temp.°C.	20	30	40	50
Solubility	5·0	5·5	7·5	10·5

The solubility of the chlorate is unaffected by the small change in carbonate concentration from 5 to 7%.[167]

Na_2CO_3-H_3BO_3-H_2O. 0° to 100°C.

The solubility of boric acid in water in the presence of sodium carbonate, bicarbonate and other salts is governed by the relation: $\log S = \log S_0 + K\sqrt{c}$, where S = solubility of H_3BO_3 (g./100g. water) and c = salt concentration (g./100g. water).[168,169]

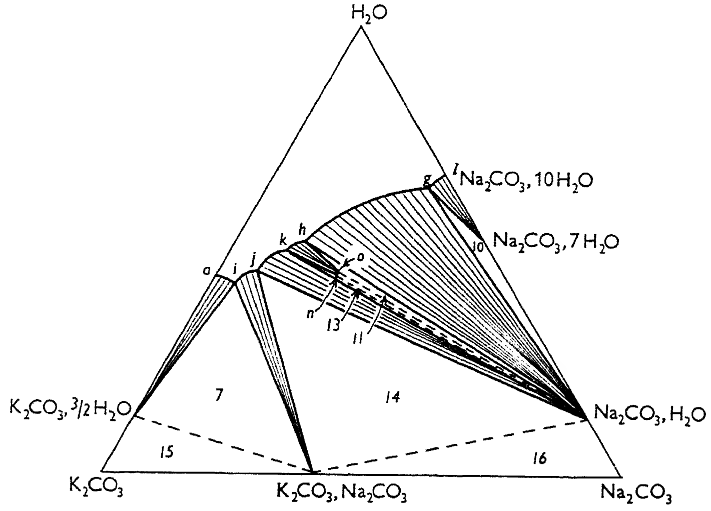

FIG. 15. 33°C. ISOTHERM FOR Na_2CO_3-K_2CO_3-H_2O

Na_2CO_3-$NaIO_3$-H_2O. 0° to 50°C., 4 Isotherms.
No double salt.[170]

Na_2CO_3-Na_2WO_4-H_2O. 19° and 29°C.

The data were used for the recovery of excess soda in the leach liquor from the autoclave-soda process in the extraction of tungsten from schulite.[171]

Na_2CO_3-Na_2SO_4-H_2O. 19·1° and 50°C.

At 50°C. there are two invariant points: the three liquidus branches are in equilibrium with three sets of solid solutions.[172] The method of spiral coordinates has been applied to plotting the densities of the solutions in the system as a fourth variable.[173] The system has also been examined at 150°, 200°, 250°, 300° and 350°C. Burkeite, $Na_2CO_3,2Na_2SO_4$ occurs as a solid phase. (Fig. 18).[54]

Some investigators have reported salts of approximate constitution Na_2CO_3, $3Na_2SO_4$ and Na_2CO_3,Na_2SO_4 but they are in fact solid solutions.

Na_2CO_3-$(NaOOC)_2C_6H_4$-H_2O. 25°, 30°, 33°, 40°C.

No compounds or solid solutions. The hydrates (deca-, hepta- and mono-) of sodium carbonate appear, as does sodium phthalate in $2C_6H_4(COONa)_2,7H_2O$. The transition temperatures of the quintuple points (deca-, hepta- and phthalate) and (hepta-, mono- and phthalate) are respectively 26·60° and 31·50°C.[174]

Na_2CO_3-H_2O_2-H_2O. 0°, 10°, 20°C.

Four compounds appear: I, Na_2CO_3,H_2O; II, $2Na_2CO_3,2H_2O,3H_2O_2$; III, $Na_2CO_3,H_2O,2H_2O_2$; IV, $Na_2CO_3,2H_2O_2$. The phases containing H_2O_2 are said to be perhydrates of sodium carbonate rather than percarbonates. There

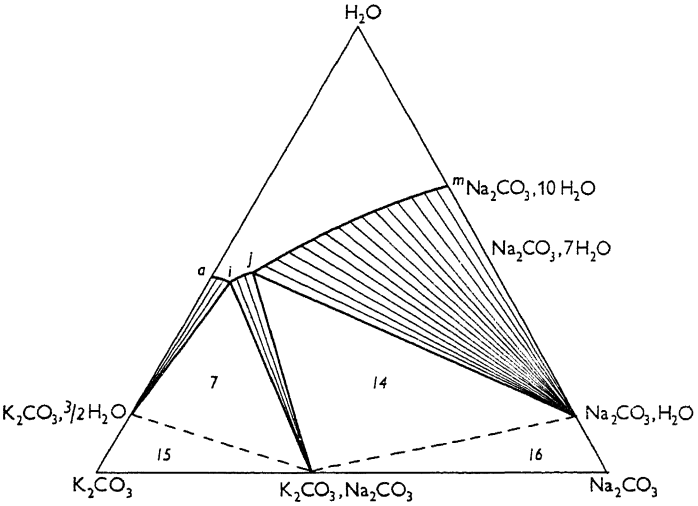
H_2O
$^m Na_2CO_3,10H_2O$
$Na_2CO_3,7H_2O$
a
i
j
7
14
$K_2CO_3,3/2H_2O$
Na_2CO_3,H_2O
15
16
K_2CO_3
K_2CO_3,Na_2CO_3
Na_2CO_3

FIG. 16. 36°C. ISOTHERM FOR Na_2CO_3-K_2CO_3-H_2O

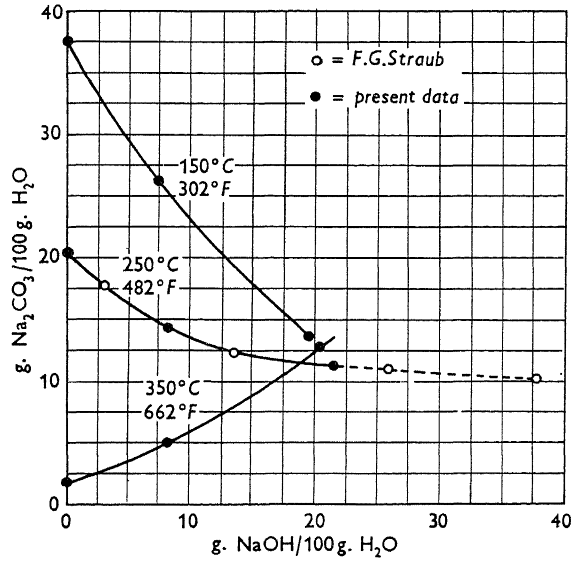

FIG. 17. SOLUBILITY OF SODIUM CARBONATE IN SOLUTIONS OF SODIUM HYDROXIDE AT 150°, 250° AND 350°C.: o F.G. STRAUB; ●SCHROEDER, BERK AND GABRIEL

is no evidence for other previously reported compounds with hydrogen peroxide Na_2CO_3,H_2O,H_2O_2; $Na_2CO_3,H_2O,2{\cdot}5H_2O_2$ and $Na_2CO_3,1{\cdot}5H_2O_2$. Anhydrous II

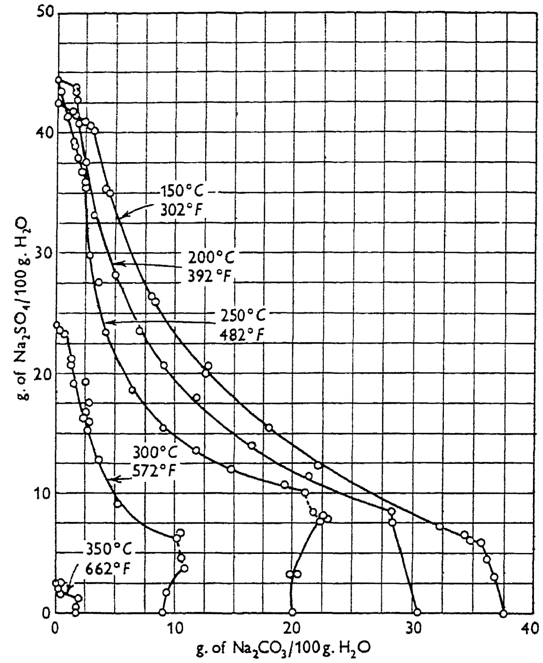

FIG. 18. SODIUM SULPHATE-SODIUM CARBONATE-WATER AT 150°, 200°, 250°, 300° AND 350°C.

and III can be obtained by heating the hydrated compounds to 105° and 95°C., respectively. IV is stable only in systems containing more than 63–64% H_2O_2 in the liquid phase at 0° or 10°C.[175,176]

Na_2CO_3–Glycerol–H_2O.

The solubility of the salt decreases considerably with increasing glycerol content. With moderate concentration of glycerol, the salt crystallizes with water as normal hydrates; at higher concentrations 'glycerolates' are said to appear. Triangular diagrams are available.[177]

(B) Water is absent.

Na_2CO_3–NaCl–KCl.

A eutonic point occurs at 660°C. with 29 mol.-% Na_2CO_3, 32 mol.-% NaCl and 39 mol.-% KCl.[4]

Na_2CO_3–K_2CO_3–$BaTiO_3$ (up to 1200°C.).

A field of crystallization of solid solutions of Na_2CO_3 and K_2CO_3 (1·27% of the area of the system) and a field of crystalline barium titanate occur.[178-180]

Na_2O–CO_2–Fe_2O_3. (Over the concentration range attainable by heating mixtures of sodium carbonate and ferric oxide).

An evolution of carbon dioxide corresponds to Na_2O,Fe_2O_3, m.p. 1345°C.; it is extremely hygroscopic. It forms a two-liquid system with sodium carbonate. The heat of reaction is given by:- $Na_2CO_3(s) + Fe_2O_3(s) \rightarrow Na_2Fe_2O_4(s) + CO_2(g)$; $\Delta H = 32{,}060$ g.-cal. and of formation by:- $2Na(s) + 2Fe(s) + 2O_2(g) = Na_2Fe_2O_4(s)$; $\Delta H = -248{,}080$ g.-cal.[84]

The vapour pressures between 480° and 880°C. give a straight-line plot against log (temperature). A small sample was used (0·1 g. Na_2CO_3, 0·18 g. Fe_2O_3 and 0·06 g. sodium ferrite) and gave the isochore:

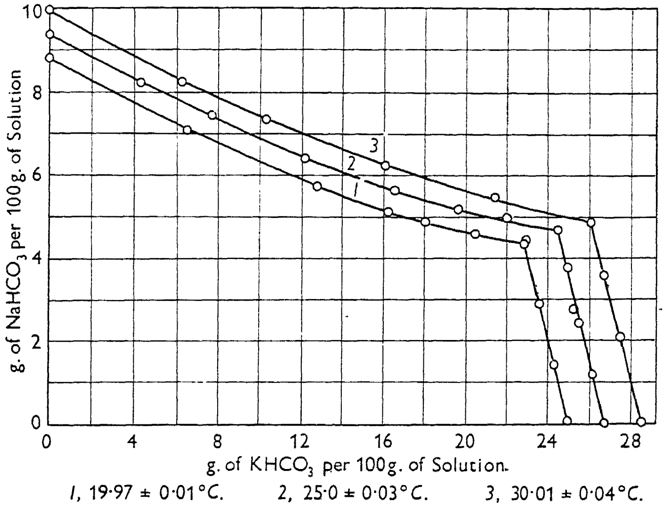

FIG. 19. COMPOSITION OF NaHCO$_3$–KHCO$_3$ SOLUTIONS

$$\log p = -7539{\cdot}6/T + 1{\cdot}75 \log T - 0{\cdot}001626\,T + 6{\cdot}0808$$

with the heat content change for the reaction $Na_2Fe_2O_4(s) + CO_2(g) \rightarrow Na_2CO_3(s) + Fe_2O_3(s)$; ΔH = −34,800 g.-cal. at 22·5°C. The Clausius–Clapeyron relation gives ΔH = −34,873 g.-cal.[181] The decomposition pressure reaches 760 mm. at 848·3°C. when ΔH = −30,038 g.-cal. and ΔS = 30·038 g.-cal./degree; $\Delta S_{298\cdot5}$ is 33·2 g.-cal./degree.

$NaHCO_3$–$KHCO_3$–H_2O. (19·97 ± 0·01°, 25·00 ± 0·03°, 30·01 ± 0·04°C.)

This system was investigated under the fixed condition that the sum of the partial pressures of carbon dioxide and water vapour is constant and equal to the atmospheric pressure. There are no hydrates, solid solutions or double salts. The only solid phases are the two bicarbonates.[127] (Fig. 19). The isotherm at 0°C. is given in another report.[182]

$NaHCO_3$–Na_2CO_3–H_2O.

The classic research on this system was carried out in connection with the ammonia-soda industry[183] and extended to the quaternary system. The temperature limits are 0° to 100°C. This paper offers an exhaustive investigation and is accompanied by many diagrams which should be consulted. (Fig. 20).

Other work[128] covers the region 100–200°C. and isotherms are given for five temperatures. (Figs. 22–24). Trona, or sesquicarbonate, is stable up to 195 ± 5°C. Wegscheider's double salt, $3NaHCO_3,Na_2CO_3$ is stable throughout the entire range. Another examination includes the region 20°–945°C. and gives results for 11 different temperatures.[184]

Two investigations [185,207] agree in certain particulars at 25°C. (Fig. 21) and differ from the earlier comprehensive work.[183] Figs. 22, 23 and 24 give isotherms for higher temperatures.[185]

Na_2CO_3–Sucrose–H_2O.

The viscosity of aqueous solutions of sucrose has been determined in the

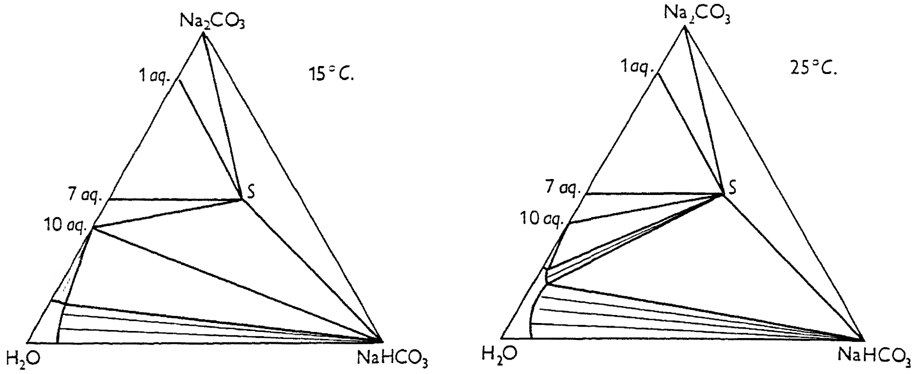
Na_2CO_3
1 aq.
15°C.
7 aq.
10 aq.
S
H_2O
$NaHCO_3$
Na_2CO_3
1aq.
25°C.
7 aq.
10 aq.
S
H_2O
$NaHCO_3$

FIG. 20. SYSTEM $NaHCO_3$-Na_2CO_3-H_2O AT 15° AND 25°C.

presence of sodium carbonate (5% addition at 20–60°C.). The viscosity decreases with temperature and increases with salt concentration.[186]

The system is of importance in the study of molasses formation. The refractive index has been used in determining the velocity of crystallization of sucrose.[187]

Na_2CO_3-Organic liquid-H_2O.

The rectilinear representations of the binodal isotherms have been examined

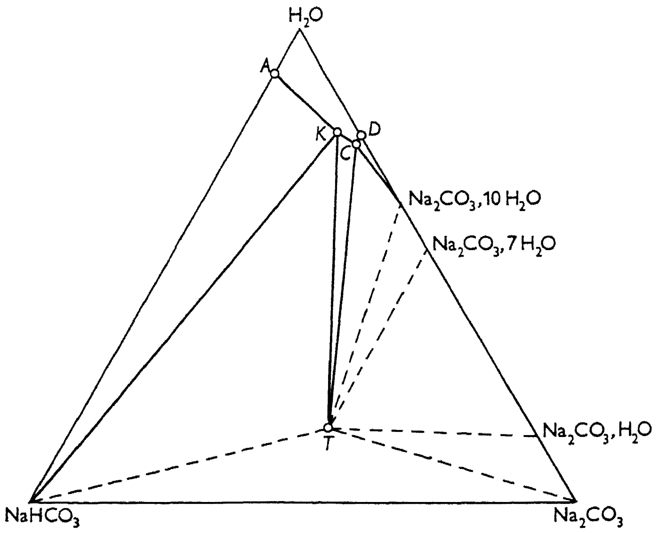
H_2O
A
K
D
C
$Na_2CO_3,10\,H_2O$
$Na_2CO_3,7\,H_2O$
T
Na_2CO_3,H_2O
$NaHCO_3$
Na_2CO_3

FIG. 21. ISOTHERM FOR $NaHCO_3$-Na_2CO_3-H_2O AT 24·87°C.

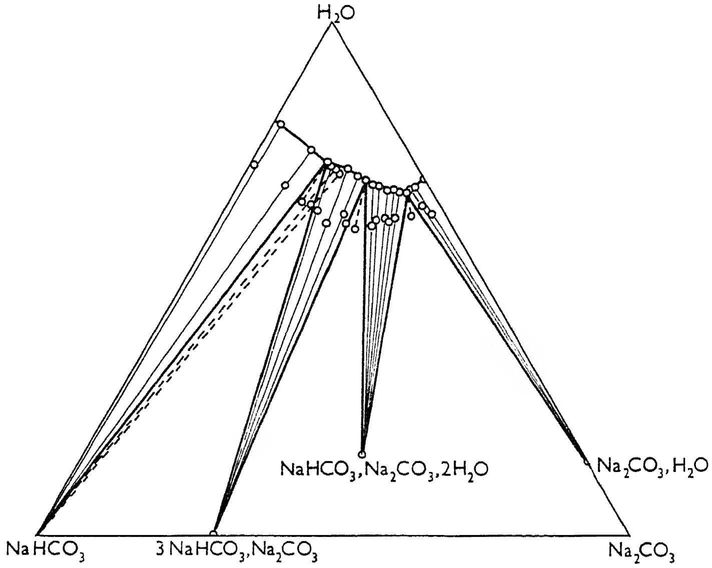

FIG. 22. ISOTHERM FOR $NaHCO_3$-Na_2CO_3-H_2O AT 100°C.

in a number of cases. The molecular concentration of the components of these systems follow the relation $m_s/m_l = (1-am_{oa})[(m_{oa}/m_a)-1]$ where a, the angular coefficient is 2·583, m_o the molar concentration of organic liquid (propyl alcohol, isopropyl alcohol, allyl alcohol, or acetone), m_l that of water, m_a that of sodium carbonate (all in 100 g. of solution) and m_{oa} is the concentration of alkali in 100 g. of saturated aqueous solution. Propyl alcohol was used in a much earlier investigation.[188]

The systems Na_2CO_3-tertiary butanol-H_2O[190] and Na_2CO_3-isopropanol-H_2O[189] have been more fully examined. The ratio of the concentration of alcohol to that of water in the salt-rich phase is probably the best measure of the salting-out efficiency; the smaller the ratio the more efficient is the salt. Data are given for points on the binodal curve; it is sufficient to cite here (Table XXII.) some of the conjugate points. (*A* = wt.-% of alcohol in the alcohol-rich phase, *B* = wt.-% of sodium carbonate in the salt-rich phase, P.P. = plait point).

TABLE XXII.- CONJUGATE POINTS ON THE BINODAL CURVES IN ALCOHOL-SODIUM CARBONATE-WATER SYSTEMS

*iso*Propanol, 25 ± 0·2°C.		Tertiary butanol, 30 ± 0·2°C.	
A	*B*	*A*	*B*
63·5	19·6	97	25·2
19·9	6·3 (P.P.)	70	7·7
1·6	0·1	55	4·5
		35	2·0 (P.P.)

It is found that if y = wt.-% of isopropanol, x = wt.-% of salt, and a, b, c are numerical constants, in the expression $y = a + b \times 10^{-cx}$, the alcohol-rich

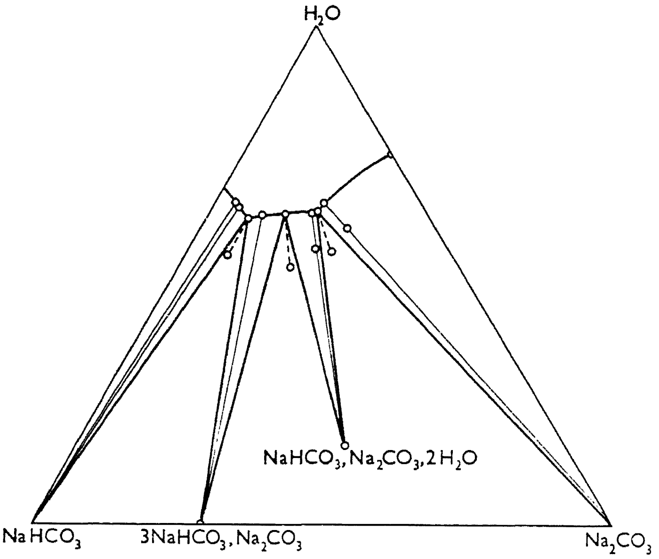

FIG. 23. ISOTHERM FOR $NaHCO_3$-Na_2CO_3-H_2O AT 170°C.

phase is given by $a = 15{\cdot}73$, $b = 51{\cdot}0$, and $c = 0{\cdot}1725$, and the salt-rich phase by $a = -2{\cdot}55$, $b = 49{\cdot}4$, and $c = 0{\cdot}0538$.

Reciprocal Salt Pairs.

In such a system as $CaCrO_4 + Na_2CO_3 \rightleftharpoons Na_2CrO_4 + CaCO_3$, conventionally represented as Ca,2Na||CO_3,CrO_4, the relation established by the equation removes a degree of freedom and although there are four components the system is ternary. These systems of reciprocal salt pairs are of importance in industrial processes. The change in heat content is given where available. Its significance has been discussed with relation to the reversibility of the reactions.[191]

Ca,2Na||CO_3,CrO_4.

Explored by thermal analysis in an atmosphere of carbon dioxide and the solid phases identified optically. There are five crystalline regions where the solid phases are respectively $CaCrO_4$, $CaCO_3$, Na_2CO_3,$CaCO_3$, and solid solutions (i) of $CaCrO_4$ in Na_2CrO_4 and (ii) of $CaCO_3$ in Na_2CO_3. Three quaternary eutectics occur near 650°C.[51]

2Li,2Na||2OH,CO_3.

$$2LiOH + Na_2CO_3 \rightleftharpoons Li_2(CO_3) + 2NaOH; \quad \Delta H = -4300\text{ g.-cal./mole}$$

2Na,2K||2OH,CO_3.

$$\Delta H = -2100\text{ g.-cal./mole.}^{191}$$

Na,K||Br,½CO_3.

$$\Delta H = -1800\text{ g.-cal./equiv.}^{60,142}$$

Two fields of solid solutions (of carbonates and bromides) occur.

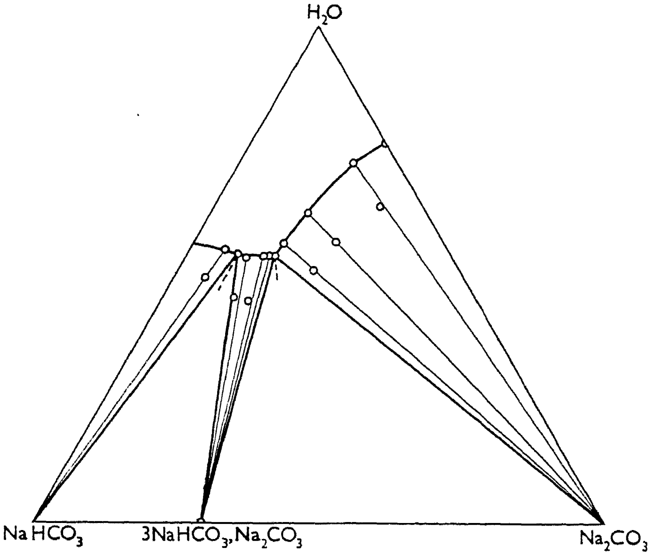

FIG. 24. ISOTHERM FOR $NaHCO_3$-Na_2CO_3-H_2O AT 200°C.

Na,K||I,½CO_3.

$$\Delta H = -4{\cdot}90\,\text{kg.-cal./equiv.}^{60}$$

Ca,2Na||MoO_4,CO_3 (in water).

This gives the gram-ratio Na_2MoO_4/Na_2CO_3 = 2·1 at 25°C. at equilibrium. The percentage of $CaMoO_4$ dissolved by aq. Na_2CO_3 is 3·9. The equilibrium was approached from the calcium molybdate side;[192] attempts to establish equilibrium from calcium carbonate and sodium molybdate were unsuccessful.

2Na,2K||2Cl,CO_3 (in water), and

2Na,2K||SO_4,CO_3 (in water).

Tables and graphs are available; the compositions of solutions saturated at 25°C. are given.[24]

2Na,2NH_4||SO_4,2HCO_3 (in water at 30° and 40°C.)

(Under the corresponding decomposition pressure of the saturated solution of NH_4HCO_3).[193,194] At 0°C. there are five crystalline fields. That of $NaHCO_3$ decreases as the temperature falls.

Ca,2Na||CO_3,SO_4 (in water).[195]

Concentrations ranging from 0·01 to 0·002 g.-mol./l. at ordinary temperatures.[196]

Na,NH_4||Cl,HCO_3 at 20°, 30°, 40° and under p_{CO_2} = 1·2 and 2·5 atm.[197]

A partial examination of the equilibria in the ammonia-soda process under pressure.

2Na,2K||2ClO_3,CO_3 (in water, 24·2° and 40°C.).

At 24·2°C. the solid phases may be $KClO_3$,$NaClO_3$, Na_2CO_3,7H_2O, Na_2CO_3,10H_2O, K_2CO_3,2H_2O, K_2CO_3,Na_2CO_3,6H_2O. With the ternary system $NaClO_3$–

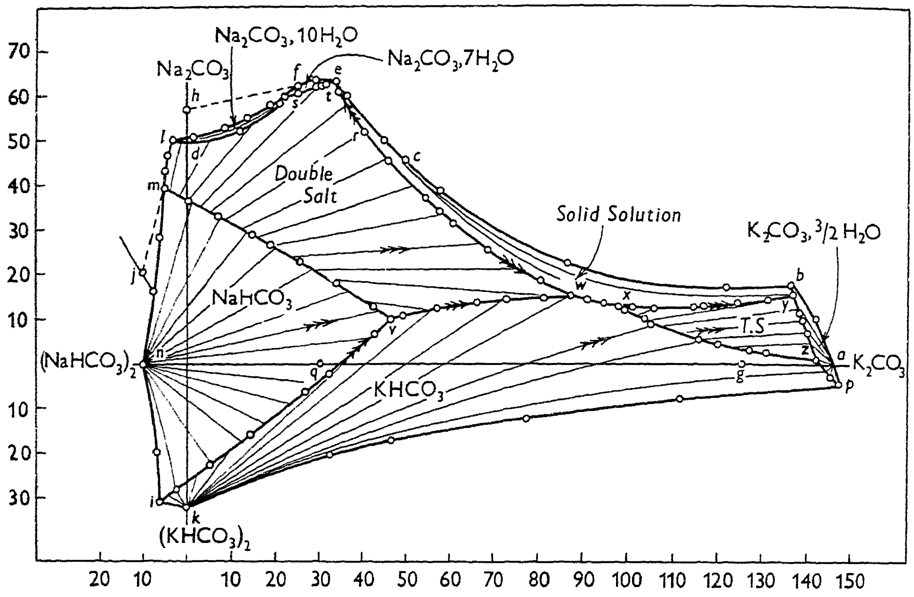

FIG. 25. K_2CO_3-$NaHCO_3$-Na_2CO_3-$KHCO_3$-H_2O AT 25°C.

Na_2CO_3-H_2O the solid phases are at 24·2°C. $NaClO_3$, $Na_2CO_3,7H_2O$, $Na_2CO_3,10H_2O$: the formation of the heptahydrate below its transition point is attributed to the removal of available water by sodium chlorate. At 40°C. $NaClO_3$ and Na_2CO_3,H_2O are the solid phases. The ternary system K_2CO_3-Na_2CO_3-H_2O was examined at −6°, 10°, 24·2° and 40°C.: at −6°C. a new double salt hydrate $Na_2CO_3,K_2CO_3,24H_2O$ is said to separate.[72]

Quaternary and Multi-component Systems.

Na_2CO_3-$NaNO_2$-$NaNO_3$-H_2O.

Isotherms in the range 10–30°C. show that the equilibrium concentrations of nitrite and nitrate diminish as the percentage of sodium carbonate in the solution rises from 0 to 4%.[161]

$NaHCO_3$-$NaCl$-$MgCO_3$-H_2O.

Of interest in brine purification; NaCl, $Na_2CO_3,MgCO_3$, $Na_2CO_3,MgCO_3$ appear.[48]

Na_2CO_3-H_2Se-Se-H_2O (CO_2).

Selenium dissolves in sodium carbonate solution into which hydrogen selenide has been passed to give Na_2Se_x. For 0·002 mole of H_2Se in 20 ml. of sodium carbonate solution the maximum value of x is 3·2 for concentrations

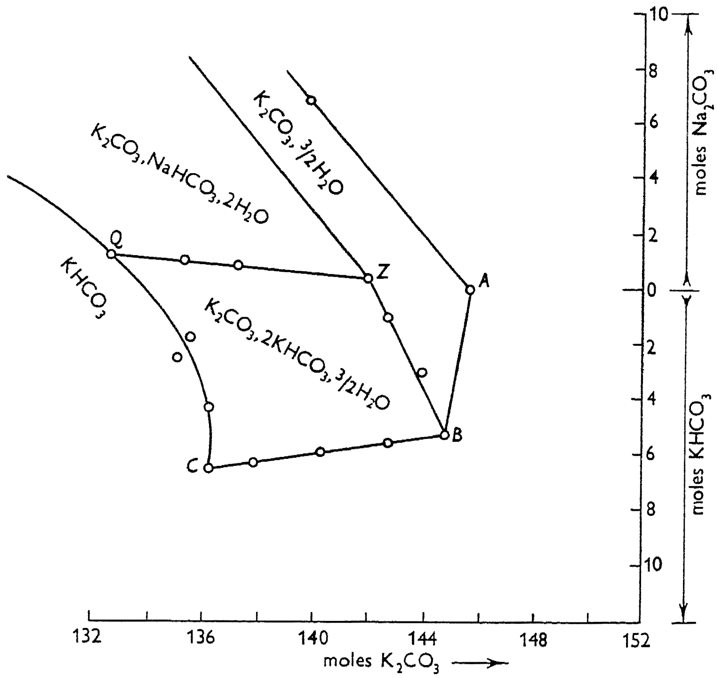

FIG. 26. SYSTEM K_2CO_3-$NaHCO_3$-Na_2CO_3-$KHCO_3$-H_2O AT 25°C.

of carbonate from 0·5 to 1·6 M. Smaller concentrations of H_2Se give higher values of x, lower temperatures give lower values of x. At low temperatures and low concentrations Na_2Se_2 is the main product but as temperature and concentration of carbonate rise, Na_2Se_3 and Na_2Se_4 take preference.[198]

Na_2O-BaO-SiO_2-CO_2.

Partly investigated in the solid reactions between quartz, barium carbonate and sodium carbonate in the solid state.[199]

Na_2CO_3-$NaCl$-$NaOH$-H_2O.

Studied at 100°C.: there is a transition point at 11·07% NaOH, 4·93% Na_2CO_3, 16·89% NaCl with Na_2CO_3NaCl and Na_2CO_3,H_2O as solid phases.[52]

$Na^+,NH_4^+||HCO_3^-,OH^-$-$H_2O$.

Studied at 35°C. to determine the boundaries of crystallization of sesquicarbonate in the presence of ammonium ion; the volumes of this salt and of bicarbonate are significantly expanded according to the amount of saturation by ammonia.[71]

$NaHCO_3$-Na_2CO_3-Na_2SO_4-H_2O.

Plotted on 'spiral coordinates'.[173] Examined at 25°C. Three solid phases in equilibrium: $Na_2CO_3,NaHCO_3,2H_2O$, $Na_2CO_3,10H_2O$ and $Na_2SO_4,10H_2O$.

Na_2CO_3-Na_2SO_4-$NaOH$-H_2O.

Solubility data are given for concentrations of caustic soda from 5 to 60% and for temperatures from 50° to 140°C.[200] Four fields at 100°C.: Na_2SO_4, Na_2CO_3, Na_2CO_3,H_2O and $2Na_2SO_4,Na_2CO_3$.[52] Data for two concentrations of sodium hydroxide are available at 150°, 250° and 350°C.[201]

Na_2CO_3-K_2CO_3-$NaHCO_3$-$KHCO_3$-H_2O (25°C.).

A new 'tetragene' salt $K_2CO_3,NaHCO_3,2H_2O$, appears.[75]

The heterogeneous equilibria at 25°C. are shown in Fig. 25 for the whole region[75] and expanded to indicate the trona area in Fig. 26.[208]

Na_2CO_3-$NaHCO_3$-$NaCl$-H_2O.

Data are available at three temperatures between 20° and 94·5°C.[184]

Na_2CO_3-$Na_4Fe(CN)_6$-Na_2SO_4-H_2O and

Na_2CO_3-$Na_4Fe(CN)_6$-$NaCl$-H_2O.[202]

Na_2CO_3-$NaHCO_3$-NaF-H_2O.

The 'mutual solubilities' at various concentrations and temperatures have been determined.[203]

Na_2CO_3-H_2S–CO_2-H_2O.

Arises in the removal of hydrogen sulphide and carbon dioxide from industrial gases by absorption in dilute aqueous carbonate.

The essential reactions are:

$$Na_2CO_3 + H_2S + H_2O \rightarrow NaHCO_3 + NaHS + H_2O \ (\textbf{A});$$
$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \ (\textbf{B});$$
$$NaHS + CO_2 + H_2O \rightarrow NaHCO_3 + H_2S \ (\textbf{C}).$$

The relation between the vapour pressure of hydrogen sulphide, P, and its concentration (c) in a N. solution of carbonate at equilibrium from 20–60°C. is $P = 5{\cdot}4(t + 48)c^{3{\cdot}04}$. Hydrogen sulphide in N. sodium carbonate (equilibrium **A**) is determined by the empirical expression $K_1 = [NaHCO_3][NaHS]/[Na_2CO_3]\,P_{H_2S}$. At 25°C. $K_1 = 0{\cdot}048$ moles/l.mm.; and $\log K_1 = (2500/4{\cdot}596\,T) - 3{\cdot}16$. For simultaneous absorption of hydrogen sulphide and carbon dioxide by an aqueous solution of sodium carbonate, equilibrium in the system H_2S–CO_2–Na_2CO_3–$NaHCO_3$–$NaHS$–H_2O is determined by K_3, which is the ratio of the equilibrium constants K_1 and K_2 in the systems H_2S–Na_2CO_3–$NaHCO_3$–$NaHS$–H_2O and CO_2–Na_2CO_3–$NaHCO_3$–H_2O, K_2 being $[NaHCO_3]/[Na_2CO_3]P_{CO_2}$. K_3 is of the order of unity and the variation of free energy for this reaction has the order zero; the process is therefore easily reversible for standard conditions, and small deviations from these may greatly affect the course of the process. To get the minimal absorption of carbon dioxide, it should be carried out at the highest possible temperature.[204]

Na_2SO_4–Na_2CO_3–$NaCl$–$NaOH$–H_2O (100°C.).

Contrary to previous investigations, Na_2CO_3,H_2O is not found as a solid phase over the entire range of sodium hydroxide concentrations. Two points occur with three solid phases, Na_2SO_4, $NaCl$ and $2Na_2SO_4,Na_2CO_3$, and one point with four solid phases, Na_2CO_3, Na_2CO_3,H_2O, $NaCl$ and $2Na_2SO_4,Na_2CO_3$.[52,201]

$2Na^+,2NH_4^+||2HCO_3^-,2OH^-,SO_4^{--},$–$H_2O$ (35°C.).

This five component pseudo-quaternary system develops from the reciprocal salt pair by the inclusion of sulphate ion. The field of observation is further restricted by the complexity to the ratio $(2HCO_3^-)/SO_4^{--}$ 2 or 0·5. Again in the quinary system in the presence of SO_4^{--} the fields of $NaHCO_3$ and sesquicarbonate are expanded according to the amount of saturation by ammonia.[71]

$Na^+,NH_4^+||Cl^-,OH^-,HCO_3^-,$–$H_2O$.

This five-component system has been completely explored at 30°C. and partly at temperatures ranging from 0° to 60°C.; it is considered more fully in the section on the Solvay process. The included reciprocal salt pairs:

$$NaCl\text{-}NH_4OH\text{-}NaOH\text{-}NH_4Cl \quad (i)$$
$$NaCl\text{-}NH_4HCO_3\text{-}NH_4Cl\text{-}NaHCO_3 \quad (ii)$$
$$NaOH\text{-}NH_4HCO_3\text{-}NH_4OH\text{-}NaHCO_3 \quad (iii)$$

as well as the ternary systems:

$$NaCl\text{-}NaOH\text{-}NaHCO_3 \quad (iv)$$
$$NH_4Cl\text{-}NH_4OH\text{-}NH_4HCO_3 \quad (v)$$
$$NaCl\text{-}NH_4OH\text{-}NH_4HCO_3 \quad (vi)$$

are examined at 30°C. for various water contents in aqueous solution.[205] Much published information on the salt pairs (ii) and (iii) is indeterminate with respect to the degree of bicarbonation, the partial pressures of ammonia, carbon dioxide and water vapour being very high in parts of the system.

$H_2NCOONH_4$-$H_2NCOONa$-NH_4Cl-$NaCl$-NH_3.

The system is of importance in the manufacture of sodium carbonate by precipitation in liquid ammonia. No details are given but the method of analysis is described.[206]

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THE ELECTRICAL PROPERTIES OF SODIUM CARBONATE AND BICARBONATE

Ionic Equilibria.

The hydrolysis constant for sodium carbonate has been re-determined from adsorption measurements on quartz in aqueous solutions of carbonate and hydroxide; it is given by the expression $K_n = [2c'(c'+x)/(c-x-2c')] \times 10^{-2}$, where c is the concentration of dissolved hydroxide, c' the entire alkali titre of the solution after adsorption and x the concentration of adsorbed hydroxide. K_n was found to be $3{\cdot}4 \times 10^{-4}$ at 25°C.[1] a much earlier value[2] being $1{\cdot}9 \times 10^{-4}$. In this connection it may be recorded that K_2 for H_2CO_3 at 18°C. is $6{\cdot}2 \times 10^{-11}$ and the second hydrolysis constant is therefore $1{\cdot}03 \times 10^{-4}$. These data were obtained in an investigation of the reaction $2Na_2CO_3 + 4HBO_2 \rightleftharpoons 2NaHCO_3 + Na_2B_4O_7 + H_2O$ and it is shown that the equilibria borax-bicarbonate $\rightleftharpoons$ boric acid-carbonate and borax-carbonic acid $\rightleftharpoons$ bicarbonate-boric acid may be disregarded.[3]

Hydrogen Ion Concentration.

The aberration of the practical pH scale near its ends arises from the definition in terms of the e.m.f. of the cell Pt; H_2(g.), soln.|satd. KCl| standard, H_2(g.); Pt, the pH being usually obtained from the difference of two e.m.f. values for a cell with glass and calomel electrodes, one of which is a calibration with a standard of known pH. Junction potential errors arise, and the glass hydrogen electrodes lack correspondence in hydrogen-ion activity at the extremes of scale. Adjustments made with present standards will usually be 0·02 to 0·05 below correct pH above pH = 11, and ± 0·03 below pH = 2·5. At 25°C., 0·025 M.$NaHCO_3$ + 0·025 M.Na_2CO_3 has pH = 10·02 and is suggested as one of five additional standards. The pH of aqueous sodium carbonate solutions of different normalities is:[4]

N.	1·000	2·000	3·000	4·000	5·000	6·000
pH	12·27	12·49	12·63	12·73	12·78	12·80

Another investigation uses a glass electrode in the determination of pH values of solutions of carbon dioxide and of sodium bicarbonate for titration of such solutions with sodium hydroxide or sodium carbonate.[5]

A systematic study of pH values of solutions of phosphate, borate, carbonate and bicarbonate of sodium in mixtures and with added hydroxide has been made. With the bicarbonate pH decreases with rise in temperature and shows a maximum at low concentrations.[6] The following values are given at 30°C.

Concn. in moles/l.	0·05	0·10	0·20	0·30	0·40	0·50
Na_2CO_3	11·16	11·28	11·41	11·48	11·62	11·66
$NaHCO_3$	8·35	8·32	8·26	8·23	8·21	8·15

An interesting phenomenon has been noticed in glass electrodes. A freshly blown bulb appears to be filled with an aerosol of sodium carbonate which sediments after some hours and forms complicated patterns on the inside of the bulb. The asymmetry potential of glass electrodes, which diminishes on prolonged immersion in water, is probably due to unequal loss of sodium from the internal and external surfaces.[7]

A sodium carbonate-bicarbonate buffer suitable for alkaline phosphatases can be prepared from mixtures of decimolar solutions to cover the range pH = 9·16–10·83 at 20°C. and 8·77–10·57 at 37°C. They are reasonably stable.[8] The drop in pH with rise in temperature has some importance in the admixture of soda with synthetic detergents; the pH of a 1% solution of soda ash drops from 11·1 at 16°C. to 10·0 at 85°C.[9]

The pH of sodium carbonate solution is decreased by the addition of polyols, the order of effectiveness being glucose, sucrose, glycerol and glycol, proportional to the amount added.

Conductivity of Sodium Carbonate Solutions.

Earlier data were not corrected for the hydrolysis of sodium carbonate; new determinations give the mobility of the carbonate ion as 69·3 ± 0·3 at 25°C., and up to $C = 0{\cdot}005$, the equivalent conductivity is $\Lambda = 109{\cdot}4 - 152C^{0{\cdot}5}$. The limiting Onsager equation is $\Lambda = 119{\cdot}4 - 174C^{0{\cdot}5}$.[10] It has been shown that solutions of electrolytes may be evaporated by passing a.c. through them and using them as resistances to give uniform heat throughout, and solutions of salts having a negative temperature coefficient of solubility may be concentrated if the electrodes are kept slightly cooler than the solution. In the course of the experiments the specific conductance of a saturated solution of sodium carbonate in mhos per cm. cube was determined;[11] data are given in Table XXIII. Values for lower concentrations appear in Table XXIV.

TABLE XXIII.- SPECIFIC CONDUCTANCE OF SATURATED SODIUM CARBONATE SOLUTION (mhos per cm. cube)

Temp.°C.	Sp. conductance
25·0	0·103
27·6	0·0984
30·0	0·0991
34·8	0·102
42·8	0·134
50·0	0·167
64·0	0·234
75·0	0·286
90·0	0·366

The conductivity of a number of electrolytes has been measured under fairly

TABLE XXIV.- SPECIFIC CONDUCTANCE OF SODIUM CARBONATE SOLUTION[12]
(mhos per cm. cube)

Concentration	t = 25° C.	t = 35° C.
1·000 N.	0·05305	0·06490
2·000 N.	0·08058	0·09997
3·000 N.	0·09656	0·1211
4·000 N.	0·1027	0·1311
5·000 N.	0·1016	0·1298
6·000 N.	0·09526	0·1250

high pressures. The relative resistance R_p/R decreases rapidly with increasing pressure in the case of weak electrolytes; strong electrolytes show a minimum except sodium chloride, which gives a continuously increasing ratio. The results for sodium bicarbonate are interesting and are given in Table XXV. (R_p = resistance at pressure p kg./cm.^{2}, R_1 = resistance at 1 kg./cm.^{2}).

TABLE XXV.- RELATIVE RESISTANCE OF SODIUM BICARBONATE SOLUTION UNDER PRESSURE[13]
(DILUTION v = 100)

p(kg./cm.^{2})	R_p/R_1		
	t = 20° C.	40·07° C.	60·27° C.
1	1·000	1·0000	1·0000
500	0·9687	0·9813	0·9892
1000	0·9528	0·9762	0·9892
1500	0·9452	0·9744	0·9933
2000	0·9452	0·9790	1·0000
2500	0·9528	0·9864	1·0082
3000	0·9623	0·9960	1·0206

Some data are available for the conductivity of dilute aqueous solutions in the presence of sucrose (15·89 and 26·03 g. per 100 ml.). There seems to be a general tendency among the salts investigated for the range of agreement with the modified Kohlrausch relation ($\lambda = \lambda_\infty - a\sqrt{C}$) to widen in more concentrated sucrose solutions.[14] Similar work has been done on mixtures of glycocoll with salt solutions including sodium carbonate; the conductivity generally decreases except for bivalent cation + multivalent anion and tervalent cation + quadrivalent anion.[15]

A relation between the conductivity and the vapour pressure of a solution has been calculated from data in Landolt–Börnstein. It is:

$$K \log (p_0/p) + rC = nF,$$

where K is a constant depending on the temperature of the solution, p_0 and p are the respective vapour pressures of water and the solution, r a constant specific to the solute, C the electrical conductivity, n the concentration in moles/100 g. of water, and F another constant specific to the solute but expressing in some way the relationship of the solute to the solvent. At 100° C. K is 3926, and for sodium carbonate r and F are respectively 76 and 75.[16]

The specific conductivity of molten sodium carbonate is given in Table XXVI.

Sodium carbonate melts between 835° and 850° C. Mixtures of sodium carbonate and sodium chloride, although completely miscible in the molten state, show anomalous conductivity behaviour; in particular the curve for $4NaCl:1Na_2CO_3$ shows marked breaks at 740°, 850° and 1000° C.[17]

The conductivity of a bunsen flame has been determined from the resistance of a condenser in the flame, by both a.c. and d.c. methods, which give

TABLE XXVI.- SPECIFIC CONDUCTIVITY OF MOLTEN SODIUM CARBONATE
(mhos per cm. cube)

Temp.°C.	830	835	850	860	875	900	960	1000	1020	1030	1050
Sp. conductivity	1·60	1·64	2·37	2·58	2·64	2·69	2·76	2·84	2·92	2·82	2·84

comparable results. The conductivity of the pure flame is $\lambda = 21{\cdot}8 \times 10^4$ sec.$^{-1}$.; with the introduction of sodium carbonate λ rises to 1640×10^4 sec.$^{-1}$. λ is determined from the expression $\lambda = K/R$ where R is the resistance and K the capacity of the flame condenser (0·159/cm.)[18]

Electrolysis of Soda Solutions.

If pure molten sodium carbonate is electrolyzed with a graphite anode open to the air, the first anodic reaction mechanism is $C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e$. The cathodically deposited alkali, however, reacts with oxygen and the oxides diffuse to the anode, so that $C + 2CO_3^{2-} + 2Na_2O \rightarrow CO_2 + 2Na_2CO_3 + 4e$. With a small anode the maximum current density values are related to the temperature by $\ln(\text{c.d.}) = (A/T) + B$, where T is the absolute temperature, A is a function of the potential, and B is a constant.[19] The a.c. electrolysis of sodium carbonate solutions at voltages as high as 110, even with arcing on the electrodes, does not give carbon dioxide; with aqueous bicarbonate and platinum electrodes hydrogen, oxygen and carbon dioxide are freely evolved until the bicarbonate has been completely transformed to carbonate, when the evolution of carbon dioxide ceases. During the electrolysis finely divided platinum is deposited on the electrodes and inhibits the evolution of the gases but does not affect the current flow. The decomposition potential of bicarbonate solutions with respect to the evolution of carbon dioxide (smooth platinum, d.c.) is 2·2 V., and that of carbonate solutions, 3·5 V. The anodic discharge potential of bicarbonate is −1·45 to −1·50 V., and of carbonate −1·90 to −1·95 V.[20] The decomposition potential of fused sodium carbonate is 2·0 to 2·1 V.[21] An equation has been derived for the calculation of current distribution from the conductivity and the current density–potential curve, and tested with reasonable results with sodium carbonate and other solutions. The effect of cell geometry and electrode shape was established empirically. The nature of the electrolyte has no effect.[22]

Polarization curves recorded with solutions of sodium bicarbonate and other salts through which a current of purified carbon dioxide is passing support the belief that the gas can be reduced at a mercury cathode, and electrolysis experiments at various current strengths yield formic acid as the only detectable reaction product, often approaching 100% current efficiency.[28]

In glow electrolysis (anode in the solution and cathode above the surface) sodium bicarbonate, unlike caustic potash and sulphuric acid, remains unchanged. It has been suggested that the bicarbonate reacts with hydrogen atoms to yield hydrogen gas and sodium percarbonate, $Na_2C_2O_6$, part of the liberated oxygen remaining in the solution. The percarbonate hydrolyzes back to bicarbonate and hydrogen peroxide.[30] The mechanism of electron transfer appears to be through water molecules of the gas phase.[31]

A solution containing 120 g. of Na_2CO_3 and 30 g. of $Na_2B_4O_7$ per litre under specified conditions produces sodium perborate; addition of $NaHCO_3$ (20 g./l.) and of some other salts increases the perborate yield by inhibiting decomposition.[24]

The possibility of using soda instead of salt for industrial electrolytic alkali has been investigated. Such a solution should give free alkali at the cathode and bicarbonate at the anode, but the insolubility of the bicarbonate and the rise in voltage are obstacles to the production of concentrated lyes. The formation of bicarbonate can, however, be avoided by using a second electrolyte with a common cation itself capable of furnishing free alkali at the cathode but incapable of producing temporary acidification of the anolyte.

Soluble alkali oxy-salts, such as sulphates, nitrates, chlorates, and perchlorates have been used; the formation of bicarbonate is hindered and a cathodic liquor containing as much as 452 g. of NaOH per l. can be formed. Sodium nitrate gives the purest hydroxide, with considerable improvement in current yield.[25]

Sodium may be produced electrolytically from fused soda and its mixtures with caustic or salt. A cathode of copper or copper alloy is used; the current is reversed at intervals for 2–10 sec., so coating the electrode with a thin film of oxide.[26]

The electrolysis of a solution of brine and soda with an iron anode has been proposed for the manufacture of the bicarbonate. Ferric hydroxide is also formed and the separation of the two is said to be possible by difference in density.[27]

Anodization.

In work on the carbonate anodization of aluminium alloys the effect of changes in current density, temperature and sodium carbonate concentration on the quality of the film was investigated for 'Duralumin'. The best film is obtained after 20–30 min. electrolysis in a 5 mol.-% solution.[29]

In the electrolytic oxidation of aluminium in bicarbonate solution, the time required for the formation of the oxide surface is decreased by the application of ultrasonic waves (500 kc.) but if the power is too high the oxide surface is destroyed.[23]

The anode polarization curves of a steel electrode have been measured in aqueous sodium carbonate and other salts; the differences in passivity shown in the solutions are attributed to differing anion dehydration energies and oxygen overvoltages.[32]

Sodium carbonate, in common with other alkali salts, offers protective action to metals by a passivation reaction in which the product formed adheres to the metal and reduces its potential; oxygen dissolved in the solution plays a part.[33] When sodium carbonate is used as an anodic inhibitor for iron partly immersed in 0·17 M. hydrochloric acid, intense water-line attack still occurs in the presence of oxygen without applied current, and in the absence of oxygen with applied anodic current. It is the slow replenishment of the inhibitor anion which appears to be the most important factor causing crevice or water-line attack in high concentrations of anodic inhibitors.[34] The nature of the corrosion product largely controls the form and rate of corrosion, *i.e.* generalized attack, local attack, or pitting. The latter appears to be obtained only in carbonate solutions containing chloride, which in low concentrations appears to reduce greatly the internal resistance of the corrosion cells.[35] In the special case of aluminium in sodium carbonate solution, the attack on anodic zones exceeds general corrosion and cracking always takes place.[36]

Examination of the water-line effect indicates that with progressive addition of inhibitor (sodium carbonate or other) the corrosion changes from general to localized and then to complete immunity, but with serious pitting at breaks in the scale, as observed in other work. The quantity required to give immunity is greater for rusted metal and is reduced by agitation. Sodium carbonate and other alkaline inhibitors should therefore be added in sufficient amounts to neutralize any acidity but not enough to cause pitting.[37]

The necessity for duplicating in laboratory tests the time of exposure and the temperature obtained in practice is stressed, many reported results being inadequate in these respects.[38]

Iron electrodes partly immersed in sodium sulphate solution in air exhibit a drop in potential of as much as 0·2 V. The immersed portion partly dissolves with formation of ferrous sulphate, whereas the emergent portion acquires an alkaline reaction due to the formation of sodium carbonate, which may be scraped off as crystals. An excess of carbon dioxide in the air favours the reaction, which is adversely affected by the presence of Mg^{2+} in the electrolyte. The carbonate appears to be formed by the action of local currents if the plate is partly covered by a thin layer of oxide; the bare spot where the iron dissolves is negative, the spot covered with oxide is positive. If the thin layer of oxide is continuous no rusting takes place. If the whole is enclosed the carbonate gradually falls off into the electrolyte, sulphate is converted into ferric oxide (carbon dioxide being released), and the continuance of the reaction is assured.[39]

The corrodibility of aluminium by alkaline salts and soaps in the presence of copper, tin, zinc, iron or magnesium is in the order of the potential series, except for sodium carbonate and zinc, which have a protective action.[40]

The irreversible electrode potential of iron in a solution containing NaCl 25, Na_2SO_4 57·5 mg./l., with 164·3 mg./l. of sodium carbonate as an inhibitor, becomes increasingly negative over a period of twelve hours. The potential/time curve shows two arrests, one at −120 mV. on the hydrogen scale, the other later at about −430 mV. Along the first portion the potential is determined by the reduction of oxygen, which causes strong concentration. Along the second branch it is determined by the anodic process $Fe \rightarrow Fe^{2+} + 2e$.[41]

Cast iron and cast steel resist soda liquors.[42]

Pure aluminium is so strongly active in 0·1 N. caustic soda that it cannot be passivated by anodic treatment. In sodium carbonate solutions the redissolving power of the solution is so small that passivity is easily obtained.[43]

Better protection is afforded by agar-agar or gum arabic than by sodium silicate, but soda is much the best.[44]

The presence of carbonate or bicarbonate decreases the concentration of chromate needed for the protection of iron from general corrosion.[45]

Cells with Sodium Carbonate as Electrolyte.

The following concentration cells have been studied, mainly for the determination of thermodynamic quantities:-

(i) $Ag_2CO_3,Ag|Na_2CO_3(0{\cdot}1\ M.),NaHg,\ Na_2CO_3\ (m_2)|Ag_2CO_3,Ag$. The e.m.f. in mV. varies from −18·7 for $m_2 = 0{\cdot}2008$ at $t = 15°C.$ to −88·6 for $m_2 = 1{\cdot}5355$ at $t = 65°C.$ The activity coefficients for these conditions were evaluated (see below).[46]

(ii) $NaHg|Na_2CO_3,10H_2O(s)$ satd. soln., $Ag_2CO_3|Ag$ (A); $NaHg|Na_2CO_3,10H_2O$ satd. soln. (no solid) $Ag_2CO_3|Ag$ (B).

For 0·206% sodium amalgam, $E_A = 2{\cdot}34804 - 0{\cdot}00357(t-25) + 0{\cdot}0000956(t-25)^2$, and $E_B = 2{\cdot}34748 - 0{\cdot}00157(t-25) - 0{\cdot}000001(t-25)^2$.[47]

(iii) $NaHg|Na_2CO_3$ aq.(m), $Ag_2CO_3(s)|Ag$. The e.m.fs were measured over the concentration range 0·001 to unit molality (m) primarily to determine the activity coefficients of sodium carbonate.[48]

(iv.) $Pt,O_2|Na_2SO_4,Na_2CO_3\ (m_1),CO_2|MgO|Na_2SO_4,Na_2CO_3\ (m_2),CO_2|O_2,Pt$. The molten electrolyte was maintained under known CO_2–O_2 pressure: a 'salt bridge' of porous magnesia connected the two half cells. The e.m.f. (E) obeyed the equation $E = (\boldsymbol{R}T/2\boldsymbol{F}) \ln (m_2/m_1)$, where m_1 and m_2 are the mol.-% of sodium carbonate; thus the electrode behaved as a reversible O_2–O^{2-} electrode, the sodium sulphate and sodium carbonate formed an ideal solution, and the junction potential was negligible.[49]

At 1227°K., with m_1 and m_2 initially 1·000 and 5·000 and finally 1·135 and 4·595, respectively, E after 8 hr. was 74·5 mV.

(v) Cells composed of silicon (less than 0·1% iron content) and other metals gave concordant results with hydrofluoric and sulphuric acids as electrolytes, but with normal sodium carbonate it was possible only to determine that graphite, silver, platinum, nickel, iron and copper were positive to silicon, whereas tin, lead and zinc were negative.[50]

(vi) The e.m.f. developed by various concentrations of aqueous sodium carbonate against normal hydrogen and calomel electrodes was measured at 25·0°C. with the following results:[12]

Normality	1·000	2·000	3·000	4·000	5·000	6·000
E.m.f.	1·00812	1·02099	1·02931	1·03489	1·03804	1·03903

General.

An interesting piece of work has been carried out with the resistance heating of metals in sodium carbonate and other electrolytes. With high voltage (200–300 V.) a gaseous shell is produced which persists for a time after the voltage is lowered and acts as a heat insulator, allowing a secondary lower voltage to be impressed, and a uniform heat treatment results with lower current consumption and density. With 15% aqueous sodium carbonate the primary and secondary voltages are respectively 220 and 100, and with 5% solution they are 300 and 160.[51]

Metallic surfaces may be electrolytically sterilized and cleaned in aqueous sodium carbonate solution; sodium hydroxide and hydrogen generated at the surface of the metal appear to be responsible.[52]

The ionization of the atomic species A and B where A = Li and B = Na has been investigated for mixtures of lithium and sodium carbonates. Under the conditions of excitation the mean concentrations were Li, $4{\cdot}33 \times 10^{17}$, Na, $1{\cdot}17 \times 10^{17}$ atoms per second. The law of mass action was shown to be valid for the ionization of atomic species in the reactions $A \rightleftharpoons A^+ + e$ and $B \rightleftharpoons B^+ + e$ with $K_A = [A^+][e]_A/[A]$, $e = [A^+] + [B^+]$, $X_A = [A^+]/[A]$ (the coefficient of dissociation of A), and $X_A/X_B = K_A/K_B$. It was found that $K_A = 1{\cdot}83 \times 10^7$ and $K_B = 4{\cdot}07 \times 10^9$, the mean observed current being $1{\cdot}75 \times 10^{13}$ electrons/sec.[53]

The Effect of Sodium Carbonate on the Luminosity and Conductivity of Flames.

The increase in the number of dispersion electrons with temperature depends on the increase in the number of normal sodium atoms, that is on the increase in dissociation of the salt. In the case of sodium carbonate, the first reaction is the complete decomposition of the salt at the flame temperature into Na_2O and CO_2, the Na_2O subsequently decomposing into sodium and oxygen atoms.[54] The conductivity of flames containing aqueous sodium carbonate spray, when compared with that given by a 'standard' solution, is found to be approximately proportional to the cube root of the concentration.[55]

Comparative measurements of the conductivity of a Bunsen flame containing sodium carbonate with a.c. and d.c. currents indicate that the same degree of accuracy is obtained in each case.[18] Mixtures of sodium carbonate, alumina and silica have been packed in a tungsten spiral to serve as the anode in a mass spectrograph. Gradual incandescence of the anode shows that sodium ions are emitted at about 800°C. The ionization potential is related to the heats of formation for Li_2O, Na_2O, and K_2O.[56] When a current is passed through a packed mass of sodium carbonate, radiations are emitted consisting of (i) a continuous spectrum between 50 and 540 A.; (ii) electrons of relatively small velocity. The electrons are emitted from the end to which they are directed by the flow of current in the substance, and have speeds corresponding to from 50 to 500 V. as the applied potential varies from 450 to 1080 V. When the applied potential is reversed positive ions are emitted. The method might be used to provide a source of slow electrons.[57]

It has been shown that the spectral distribution from zinc beryllium silicate phosphors is radically altered by small additions of sodium carbonate.[58]

Exposure to ultra-violet light for some 20 min. is said to convert sodium bicarbonate in small part to sodium carbonate with loss of carbon dioxide and water, and renders the substance nonhygroscopic.[59]

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SURFACE PROPERTIES OF SODIUM CARBONATE

The Liesegang phenomenon is exhibited by solutions of sodium carbonate of different concentrations diffusing into gelatin; or from layers of soda solution on aqueous calcium chloride with the formation of rings of opacity bands and of trees. In the latter case the necessary condition for the phenomena appears to be hydration rather than the presence of any permanent colloid; a permeable membrane of hydrocalcite, $CaCO_3,5H_2O$ forms at the boundary of the two liquids and changes gradually to a semipermeable layer of crystalline calcite. Osmosis brings about the rupture of the membrane with the formation of streamers, strata and trees. In the presence of gelatin or agar rings are formed, but no streamers, trees or opacity bands. The Liesegang phenomenon is a material record of a periodic function, *viz.* the action of a single substance upon a mobile medium capable of undergoing either structural deformation or systematic orientation. Such a medium may be a colloid or finely divided suspended matter. The substance is as a rule sufficiently strongly acidic or basic to cause a physical change in the medium. The suitable character of the substance and the condition of the medium may be developed *in situ.* Opacity bands and tree formation are special cases of the Liesegang phenomenon, the former being produced under very mild experimental conditions and the latter under the influence of forced, irregular diffusion.[1] An investigation of the influence of concentration and chemical composition of the external and internal components on the rate of diffusion, distance between layers and the periodicity constant in the phenomenon (in the absence of gelatin) was carried out at 15–17°C. for the cases of $Na_2CO_3 + BaCl_2 \rightleftharpoons BaCO_3 + 2NaCl$ and $Na_2CO_3 + HgCl_2 \rightleftharpoons HgCO_3 + 2NaCl$. The external components were saturated solutions in contact with the solid, the internal components were of various concentrations. The nature and concentration of the internal component affect the size of the periodicity constant, the distance between periodic layers, rate of diffusion and number and size of crystals deposited. Decrease of pH in an acid medium and increase in a basic medium result in a decrease in periodicity constant.[2] The periodic formation of rings has been noticed when sodium and other alkali carbonates on gelatin are placed in an electric field; the phenomenon is conditioned by the peculiar reactions of gelatin in the field.[3] If concentrated aqueous sodium or other alkali carbonate is placed on a gelatin gel, fine microscopic strata appear around the drop. Later, larger secondary rings are produced and the first fine lines disappear. The appearance is similar to microforms observed in the absence of gelatin, and thus confirms that a gel is not essential for the formation of such structures; their apparent identity with Liesegang rings suggests that the latter do not depend upon a precipitation reaction for their appearance.[4] The nature of the defomation of the rings formed by drops of saturated sodium carbonate and its antagonist on gelatin varies with the perturber; potassium ferrocyanide causes a swelling, potassium dichromate a suppression. It is supposed that the ferrocyanide favours the diffusion of sodium carbonate, whereas the dichromate restrains it. In some cases the attraction of one of the electrolytes by the other may be shown, as in the case of sodium carbonate-sodium sulphide. Around the sodium sulphide rings appear new rings with all the characteristics of those of sodium carbonate, as if the latter diffused from the centre of the sulphide drop.[5]

The type of diffusion at a membrane ('sluice' or stationary) depends very largely on the so-called W- and X-curves; these are the relations between the weights of solvent W, and of solute X adsorbed by the membrane and the proportions of W and X in the solution. The type of diffusion when the membrane is arranged as a sluice can be deduced, if the membrane is invariant, from the W- and X-curves. The type of diffusion has been examined for aqueous solutions of sodium carbonate and common organic acids with cellophane, pig's bladder and parchment membranes.[6]

Interfacial Tension and Flotation.

When a drop of water is added to 2–3 drops of petroleum by means of a glass fibre spontaneous dispersion of the water due to low interfacial tension (γ(interf.))and gravitational forces reaches a maximum in about 10 min. No dispersion occurs if the water is replaced by 0·1 N. borax (γ(interf.) = 16·5 erg/cm.^{2}), but with 0·1 N. sodium carbonate (γ(interf.) = 0·5 erg/cm.^{2}) definite dispersion takes place, the value of γ(interf.) depending on the concentration of sodium carbonate.[8] When increasing amounts of dry sodium carbonate and certain other alkali or ammonium salts are added to an oil-in-water emulsion of equal volumes of benzene and 0·3 M. aqueous sodium oleate the emulsion is broken at about 0·25 mole/l. At a slightly greater concentration (0·3 mole/l.) phase inversion occurs to give a stable water-in-oil emulsion. The hydrophilic end of the oleate is more solvated by water than is the hydrophobic end by benzene, and water is the continuous phase. Foreign salts like sodium carbonate 'dehydrate' the hydrophilic part so that its solvation is less than that of the hydrophobic radical, and benzene then becomes the continuous phase.[9] The surface tension of a 1% solution of sodium carbonate is 71·54 dynes/cm.; this is much reduced by the addition of wetting agents and the washing properties of this and other alkalis is greatly improved.[10]

The marked influence of sodium carbonate and bicarbonate on the capillary phenomena at the water–oil interface is shown for water and oils like B.P. paraffin. The volume of drops of distilled water from a given dropping pipette was at room temperature 4·14 ml. In the presence of sodium carbonate and hydroxide for total [Na$^+$] = 1/600, the volume varied continuously from 1·49 ml. (0% Na_2CO_3) to 3·10 ml. (100% Na_2CO_3); with mixtures of sodium carbonate and bicarbonate for total [Na$^+$] = 1/300, the volume changed from 1·58 ml. (0% $NaHCO_3$) to 3·76 ml. (100% $NaHCO_3$). It is suggested that the method is sufficiently refined to permit the detection and estimation of alkaline salts in water.[11]

The interfacial tension between vinyl acetate and sodium carbonate solution is the same as with water.[12]

The electrokinetic potential, or the potential difference in an electrical double layer, has been used for measuring the hydration of particle surfaces. The effects of the addition of various flotation agents such as sodium carbonate on a suspension of pure powdered dolomite, apatite etc., were compared by the potentials; these were determined by measuring the rate of electro-osmosis of the suspension, and apparently offer means for a rapid and objective determination of the optimum conditions for ore flotation.[13]

The negative ζ-potentials of lampblack, ferric oxide and powdered lignite in water, as determined by electrophoretic data, are raised by the presence of 0·02 N. sodium carbonate. Anion-active detergents (sodium dodecyl sulphate, potassium laurate, sodium alkylbenzenesulphonate) also do this, but only in the case of ferric oxide and potassium laurate is there any increase in the mobility on the addition of the detergent to the carbonate solution.[14]

The ζ-potential in electrostatic double-layers around suspended particles in an aqueous medium containing flotation agents determines an 'electrokinetic index' which is the difference in potentials (in millivolts) of the mineral surface in the flotation solutions of electrolyte alone and the collector agent plus the electrolyte. This index is governed by the ion that is selectively adsorbed in the double layer. Cationic adsorption is indicated by positive values of the ζ-potential, anionic by negative. Experimental results were determined for additions of sodium carbonate (the collectors), or silicate to powders of apatite, barite, etc. suspended in solutions containing 50 mg./l. of sodium oleate. The state of hydration of the mineral is lowest and the flotation activity highest at the isoelectric point; for the optimum efficiency of the collector reagent (sodium oleate) the carbonate must be added in such amount that the ζ-potential is reduced to zero. Minerals with negative ζ-potential usually do not show any anionic adsorption as collectors, for example nepheline ($(Na,K)AlSiO_4$) in sodium carbonate solutions containing 150 mg./l. of sodium oleate. The surface of these minerals becomes more highly hydrophilic with increasing sodium carbonate concentration; the introduction of sodium oleate does not change the ζ-potential and it is not adsorbed, the electrokinetic index is always zero, and no flotation effect is possible.[15] The electro-osmotic velocity and ζ-potential at a macroscopic glass surface in contact with an electrolyte are negative in 0•001 M. sodium carbonate but become positive on addition of 0•002 M. sulphuric acid, the sign change occurring on the acid side of neutrality.[16] A flotation method using various media (oleic acid, water glass, lead nitrate, aniline, etc.) has been successfully applied to the separation of precipitated borax or boric acid from common salt, and it is possible that the method may apply to mixtures of common salt and sodium carbonate decahydrate.[17] With the oxidation products of a sapropelite sodium chloride and bicarbonate can be completely separated.[18] The reaction between unhaired skin (collagen) and electrolytes can be studied by determining the membrane potential of the skin from the cell:

Calomel electrode|satd. KCl:skin:equilibrium
solution of electrolyte:satd. KCl|calomel electrode.

The potentials of the skin can be used to evaluate the relative adsorptions of one of the ions of the 'neutral' salt; in sodium carbonate on this basis the skin is anionphilic, in calcium chloride it is cationphilic.[19] The influence of the carbonate in modifying the orientation of collagen fibres after drying has been noted in the *X*-ray examination of the fibres.[20]

By comparing the conductivity of a suspension of glass or kaolin particles (0•6 to 3•4 μ in diameter) with that of the suspending fluid after centrifuging, the surface conductivity of the particles in sodium carbonate solution is shown to be greater than that calculated for the diffuse double layer and increases with increasing current frequency. The effect is probably due to surface capacitance.[21] An interesting effect has been observed in the adhesion of finely ground zinc sulphide particles in a 0•001 M. sodium carbonate solution to the bottom of the glass container. In small amounts the alkaline suspension exhibits strong repulsion between individual sulphide particles and the glass. The cumulative net weight of particles, however, when a larger amount of suspension settles, increases the penetration of the repulsion barriers and a compact cake is formed with good adhesion to the bottom. In the case of 0•001 M. sulphuric acid this adhesion decreases with increasing amount of suspension. In the acid suspension there is only a weak repulsion between the zinc sulphide particles, which is overcome by increasing cumulative net weight and flocculation (no adhesion) occurs.[22]

The flocculation point - the lowest salt concentration at which precipitation occurs - has been used in a study of hydroxyethylcellulose and methylcellulose. Amongst many salts of a number of different metals, sodium carbonate and bicarbonate were examined. Generally good reproducibility was obtained, and usually the salts examined followed the lyotropic series in their flocculating properties.[23]

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The following notes are reminders of the importance of sodium carbonate as a controlled source of hydroxyl ions. The effects are more fully discussed in the articles on ceramics and detergency in 'Utilization'.

As would be expected, sodium carbonate and to a less extent sodium bicarbonate, depress water-stable aggregation (flocculation) in soils.[24] The electrical resistance of sand samples which have been in contact for several hours with equal concentrations of sodium carbonate and chloride is found to be much higher with the carbonate, which is removed by the sand to a much greater extent. This partly accounts for the general acceptance that the carbonate is less toxic than the chloride to plants.[25] The static and dynamic yield stresses of bentonite and nonbentonite clays are raised by the addition of sodium carbonate (0·02–0·5%) to their aqueous suspensions. But the rate of moisture loss for the first is raised and for the nonbentonite lowered, which is held to indicate that sodium carbonate coagulates the bentonite and disperses the nonbentonite material.[26] The quantity of carbonate added requires consideration, since the viscosities of natural bentonite gels pass through a maximum with successive additions, whereas the viscosities of synthetic bentonites decrease continuously.[27] When a clay is flocculated by the addition of acid the imbibed water layer - the source of cohesion and, depending on its thickness, of a degree of softness or plasticity and extensibility - is reduced, and aggregation occurs with increased porosity. Deflocculation by sodium carbonate and other alkalis produces thicker water films and reduced porosity.[28,29] The relation of pH, time of shaking, and time and temperature of sedimentation to the flocculation factor of soils has been investigated with particular reference to the addition of sodium carbonate, silicate, oleate and other deflocculants.[30,31] The physical chemistry of casting clay products - again with sodium carbonate as the major external influence - is complicated by the occurrence of maximal and minimal effects.[32,33]

It is of interest in this connection that the reaction between sodium bicarbonate and sodium silicate to form silica gel has been utilized in strengthening and solidifying tower footings in loose sand. The gel holds the sand particles in a stable semipermanent mass that can be excavated by a conventional augur, and concrete can be poured into the bored holes without the need of forms. A mixture of 12 parts by volume of N. sodium silicate, 60 parts of water, and 28 parts of aqueous sodium bicarbonate (6·6lb./100lb. solution) gels in 45 to 60min.[34]

The adsorption of binary mixtures of sodium carbonate and other salts by charcoals shows a number of complicated effects, specific to the charcoals and to the salts.[35] When the charcoals are ashed, the sorption depends upon the properties of the water-soluble components (potassium and sodium carbonates) and not on the surface structure. If however these components are removed, the general sorption becomes adsorption and thus dependent on the surface structure.[36]

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THE INORGANIC CHEMISTRY OF SODIUM CARBONATE

Reference should be made to the section on the Utilization of Sodium Carbonate for the technical inorganic chemistry of this substance. Overlapping has been avoided as far as possible. The section on Physical Properties contains information on the hydrates, on molecular compounds and on thermodynamic relationships of soda in these and other compounds.

The Decomposition of Sodium Carbonate

The dissociation pressure of pure sodium carbonate heated in a platinum vessel is recorded (in mm. mercury) in Table XXVII.

TABLE XXVII.- DISSOCIATION PRESSURES OF SODIUM CARBONATE

t°C.	p
950°	0
1000°	1·5 ± 0·5
1100°	5·5 ± 1·0
1200°	14·0 ± 0·5
1300°	29·0 ± 1·0
1400°	66·0
1750°	760 (by extrapolation from log p/log t)

log p/log t is a straight line.[1]

We have $Na_2CO_3(s) = Na_2O(s) + CO_2(g)$; $\Delta H = 77$ kg.-cal. and for purposes of record $2Na(g) + C(gr) + {}^3/_2O_2(g) = Na_2CO_3(s)$; $\Delta H = -270$ kg.-cal. $Na_2O + H_2O(g) \rightleftharpoons 2NaOH$; $\Delta H = -46{\cdot}01$ kg.-cal. The thermal decomposition is said to become appreciable only above the melting point. The oxide formed is soluble in the melt so that the process is not univariant. As the concentration of monoxide builds up its evaporation as sodium and oxygen becomes increasingly important and a steady state is reached at about 1%.[2] Research in connection with the glass industry however seems to show that when sodium carbonate is heated in a stream of water vapour and air, decomposition occurs to an appreciable extent at 800°C. and is even detectable after heating for 1 day in air at 400°C., a much lower temperature than is characteristic of an evacuated system. The decomposition is regarded as due to reaction between sodium carbonate and water vapour in the air, reported much earlier by Mendeleev, giving free sodium hydroxide ($Na_2CO_3 + H_2O(g) \rightarrow 2NaOH + CO_2$; $\Delta H = 30{\cdot}87$ kg.-cal.) and at 800°C. equilibrium is reached at approximately 97·5% Na_2CO_3 and 2·5% NaOH, the actual amounts being dependent on the mass and depth of the charge. If sodium carbonate is required in a high state of purity it should not be heated for any appreciable time above a dull red heat (500°C.), the safe limit being regarded as 400°C.[3] The loss in weight is stated not to exceed 1·57% on heating at 1000°C. for 3hr. in platinum crucibles, while at 800°C. the loss is only 0·2%.[4] In porcelain the loss at 1000°C. and 3hr. is 39·15%.[5]

Formation of Other Carbonates from Sodium Carbonate

Magnesium Carbonate.

When a concentrated solution of soda is brought slowly into contact with one of magnesium chloride a transparent interfacial membrane appears before the precipitate is formed. Its chemical composition is close to $3Na_2CO_3, 2MgCl_2$. Diffusion occurs first, followed by the formation of the interfacial electric double layer. The transparent membrane is formed after this. The inter-liquid e.m.f. indicates the velocity of formation of the layer and the membrane.[6] After 1hr. of contact the composition ratio is $3Na_2CO_3{:}MgCl_2$, compared with a ratio before contact of 0·73:1.[7]

The reaction between magnesium sulphate and sodium carbonate is said not to take place at all at 20°C. for concentrations of magnesium present in ordinary waters and to be incomplete at higher temperatures. It does, however, greatly hinder the reaction of calcium sulphate and soda at this temperature.[8]

Barium, Calcium and Strontium Carbonates.

The solid reaction between sodium carbonate and barium sulphate is one of many considered by Tammann in his long series of researches dealing with reactions between solid bodies; he investigated the reactions between sodium carbonate and the sulphates of Group II metals.[9] Sulphates and carbonates do not form mixed crystals, and the reaction heat is very small:

System		ΔH (kg.-cal.)
2Na, Ba	CO_3, SO_4	−1·37
2Na, Ca	CO_3, SO_4	−23·0
Mg		−20·5
Zn		−22·1
2Na, Pb	CO_3, SO_4	−7·0
2K, Ba		−9·0
2K, Pb		−7·0

The velocity of the reaction does not, however, depend upon the reaction heat. An earlier investigation found no change on heating solid sodium sulphate and barium carbonate for 10 hr. at 430°C.[10] There is no change on compressing sodium carbonate and barium sulphate to 1000 atm., and the mixture has only slightly greater electrical resistance than pure sodium carbonate. If the heating of the mixture is extended, marked decomposition begins at about 550°C. and is very considerable at 600°C. (12·9% in 5 min.). The electrical resistance of a 2 mm. thick disk changes from 1×10^4 ohms at 500°C. to 300 ohms at 650°C. The lowest eutectic in the system $2NaBa||CO_3SO_4$ is at 790°C., and melting phenomena would appear to play an insignificant part. The other sulphates behave similarly except that lead sulphate shows 29·9% decomposition at the same temperature. Although potassium carbonate has a higher melting-point than sodium carbonate, (894 and 852°C.) the reaction between the former and barium and lead carbonates is much readier (22·5 and 40·9% decomposition at 600°C. for 5 min.). This is attributed to the existence of the potassium carbonate transition point at 410°C.[9]

In the analytically important conversion of barium sulphate into carbonate a 99% conversion of the sulphate into sodium sulphate is effected in 1 hr. by boiling 0·6–0·8 g. with at least 15 times the equivalent weight of sodium carbonate in 2–4 N. solution, if the precipitate is freshly prepared. Native barite takes twice as long.[11]

In another investigation it is stated that if the amount of sodium carbonate present is such that conversion of all sulphate to carbonate would give a Na_2CO_3:Na_2SO_4 ratio of 2, then some 77% of the sulphate is, in fact, converted. The reactivity, at first rapid, slackens gradually. If however the sodium carbonate:barium sulphate ratio is 8:1, then 1 hr. boiling will transform 98·78% of the latter. Commercially it therefore pays to use large excesses of carbonate, the unused portion being added to another batch.

The reaction with calcium sulphate to form calcium carbonate is even easier and more rapid. (see also Utilization). The equilibrium constant on boiling, Na_2CO_3/Na_2SO_4, is 0·032 for anhydrous calcium sulphate, against 3·07 for barium sulphate. Gypsum has an even lower value and on stirring gypsum with 2% sodium carbonate solution, the reaction is finished in 1 hr. The equilibrium constant for strontium sulphate is 0·015 and reaction with aqueous sodium carbonate is easy on warming and stirring. By using adequate amounts of sodium carbonate an analytical separation may be made of barium sulphate from calcium and strontium sulphate.[12]

The reactions between sodium carbonate and calcium chloride, calcium sulphate and magnesium sulphate in aqueous solution at different temperatures and times were further examined, the residual lime or magnesia content being determined. With ·10 milliequiv./l. solutions, the reaction with calcium sulphate was finished in 1hr. at 80°C., in 2hr. at 20°C.; the residual lime with excess soda was between 1·5 and 2·0 milliequiv./l. at 20° or 80°C.[13] The formation of vaterite - the most unstable form of calcium carbonate - is achieved at 30°C. by mixing degassed normal solutions in the presence of 10% alcohol, rapidly separating the precipitate, washing with alcohol and then ether and drying carefully.[14]

Detailed investigation of the reaction $CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4$ in concentrations ranging from 0·01 to 0·002 g.-mol./l. indicates that it is 58% reversible at ordinary temperatures and low concentrations, and that the 'constants' are not constants; the dependence of the reversibility upon the concentration is expressible only by some empirical relation.[15]

The efficient formation of calcium carbonate by the action of carbon dioxide on milk of lime requires well defined conditions. The concentration of the milk of lime should be 10%; carbon dioxide equivalent to three times the weight of lime should be passed; temperature, 20°C. The addition of formalin, or sodium carbonate or bicarbonate, has an accelerating effect and increases the sedimentation volume of the precipitated calcium carbonate.[16]

Lead Carbonate.

The equilibrium constant Na_2CO_3/Na_2SO_4 mentioned above is less than 0·01, and the conversion of lead sulphate into the carbonate is very easy.

The Reaction between Sodium Carbonate and Alumina.

Many examples of reactions between solids have followed the work cited above. On the assumption that gaseous and liquid phases play a fundamental role in the chemical transformation of a mixture of solids the mechanisms involved in such reactions may be (i) direct interaction between solid substances, (ii) processes involving the participation of a gas phase, (iii) reactions involving a liquid phase, and (iv) simultaneous action of gas and liquid phase. Of these (i) plays only a limited part, (ii) involves an initial distillation of a solid A followed by interaction between gaseous A and solid B, e.g., the formation of a spinel in which zinc oxide is gasified and then reacts with solid alumina. It is suggested that with sodium carbonate and alumina, silica and ferric oxide a eutectic mixture may be formed, the liquid giving rise to further reaction.[17] Small-scale experiments in platinum crucibles and closed tubes on the liberation of carbon dioxide from fluxes of soda and different oxides have been made at 1000°C. Beryllium oxide has no influence and no beryllium is dissolved on the fluxing of bauxites. Zinc oxide is without action. Boron trioxide probably first forms the metaborate and at equilibrium the orthoborate; similarly alumina forms $NaAlO_2$ and later Na_3AlO_3. Ferric oxide gives only sodium ferrite, $NaFeO_2$; carbon dioxide prevents the further development of the reaction. Titanium dioxide even with large excess of soda is not entirely transformed to Na_2TiO_3. Silica produces both ortho- and meta-silicate; tin dioxide gives corresponding stannates. Lead monoxide produces some Na_2PbO_2 at equilibrium.[18] The formation of Na_2O,Al_2O_3 by fusion of sodium carbonate and alumina in the molecular ratio is complete only at 1000–1100°C., and the product begins to dissociate at 1200–1300°C. With molecular ratios Na_2CO_3:Al_2O_3 of 2 and 3, the formation of the meta-aluminate is retarded, and the excess soda is volatilized.[19]

Artificial cryolite, Na_3AlF_6, can be prepared in a patented process from sodium carbonate and alumina. 100 parts of aluminium hydroxide (50% Al_2O_3) and 160 parts of sodium carbonate are treated with 1400 g. of hydrogen fluoride per cu. m. for 2 hr. in a horizontal rotating cylinder. The mass is then heated at 300°C. to give 200 parts of cryolite containing F 52·12, Al 12·12, Na 33·85, Fe_2O_3 1·30, with loss on ignition 1·51%.[20]

Sodium carbonate solution is said to react with aluminium in a first stage represented by $2Al + 2NaOH + 4H_2O \rightarrow 2Al(OH)_2ONa + 3H_2$ and carbon dioxide is evolved. The conversion to $Al(OH)_3$ is completed by caustic soda.[21] When alumina is formed by adding carbon dioxide to sodium aluminate solutions the size of the particles depends on the temperature of precipitation, characteristic for given concentrations; the Na_2O content increases with increase in temperature, concentration, time of contact of precipitate with solution, and the presence of carbonate and bicarbonate ions in the solution.[22]

It is reported that in the presence of sodium carbonate and particularly of sodium bicarbonate amorphous alumina gels are transformed at room temperature into a crystalline double carbonate of sodium and aluminium. The addition of 27 parts of bicarbonate and 73 parts of carbonate to the gel results in crystals which analyze $Na_2O,Al_2O_3,2CO_2,xH_2O$. Thermal curves obtained with a differential microcalorimeter indicate an exothermic heat of reaction; an initial endothermic effect corresponds to the solution of the gel by the salt. It is said that the double crystalline salt can also be prepared by the double decomposition of aluminium sulphate and sodium carbonate or bicarbonate.[23]

Alumina as bauxite or precipitated from aluminium salts by ammonia reacts completely with soda at 950°C. to give $NaAlO_2$. At the same temperature alumina prepared by precipitation from $NaAlO_2$ with carbon dioxide gives $NaAlO_2$ and Na_3AlO_3. Further heating converts to $NaAlO_2$ alone; the reaction is complete at 1200°C.

The Reaction between Sodium Carbonate and Boric Acid.

The evolution of carbon dioxide from boiling mixtures of aqueous sodium carbonate and boric acid has been measured. Water vapour was refluxed into the flask, while hydrogen was blown through at a determined rate. It was found that the decomposition of the carbonate was continuous and practically complete. There seem to be no special conditions for the formation of any definite compound during the process.[25]

The reaction between the solids has been followed by determining the loss of carbon dioxide from various mixtures of boric oxide and sodium carbonate on heating to 350–390°C. and above. At the higher temperatures a mixture of orthoborate (Na_3BO_3) and metaborate ($NaBO_2$) is formed and not metaborate alone as reported much earlier by Le Chatelier.[26] In the range 700–950°C. the equilibrium constants for $NaBO_2 + Na_2CO_3 \rightleftharpoons Na_3BO_3 + CO_2$ show that the orthoborate is not formed below 680°C. and that the metaborate is converted to orthoborate at higher temperatures by excess carbonate. $K = [BO_3Na_3]/[BO_2Na][CO_3Na]$ varies from 1·27 at 950°C. to 0·35 at 1750°C.[27]

The Reactions of Sodium Carbonate with Silica and other Glass-Forming Oxides.

The multifarious and complicated reactions which occur largely in glass making are treated more fully in the Sections on Utilization and Kinetics. Certain outstanding points of general inorganic interest are dealt with here.

The usual product of reaction between quartz and sodium carbonate is the metasilicate, containing SiO_3^{2-}; with a large excess of quartz disilicates ($Si_2O_7^{6-}$) and perhaps trisilicates ($Si_3O_9^{6-}$) are formed. Excess of carbonate converts metasilicate into orthosilicate (SiO_4^{4-}), the disilicate as also the trisilicate into the metasilicate at 600–900°C.[19,28]

Reaction between sodium carbonate and quartz occurs without fusion at 726–805°C. When the reactions take place in a stream of nitrogen, the size of the charge, composition of the mixture, rate of flow of the gas and duration of reaction have an appreciable effect on the reaction rate and on the nature of the product. In the presence of sufficient sodium carbonate the end product at higher temperatures is the orthosilicate, but the formation of a series of silicate ions as intermediates between the meta- and ortho-silicate by reaction of the former with soda is postulated. The rate of reaction of the quartz particle is said not to be measured by the rate of carbon dioxide evolution.[29]

The solid reactions between soda and precipitated silica gel containing 10–20% of water have been examined for a number of mixtures by differential thermal analysis. In all cases two endothermal peaks at 450–520°C. and 780°C. and two exothermal peaks at 580° and 620–700°C. were observed. When the gel is heated with soda at 200–800°C. an aggregation of fine crystals of sodium carbonate and coagulation of the silica are observed. At about 500°C. a reaction sets in with the formation of a glassy substance and fine interstitial crystals; the glassy substance is probably a mixture of cryptocrystal' and $Na_2O–SiO_2$ glass and is formed endothermally. The interstitial crystals were shown by *X*-ray powder methods to be Na_4SiO_4 and $Na_6Si_2O_7$. At 580–600°C. the crystals grew exothermally; at 600–690°C. the orthosilicate reacts with the glassy substance to form the disilicate and at 800°C. the latter dissolves endothermally in the glass and the mixture gradually becomes homogenous with the $Na_2O:SiO_2$ ratio 1:2·6 to 1:3·9.[30]

The interpretations of these solid phase reactions are varied. Much depends upon the initial compositions, the grain size, the rate of heating and the purity of the reactants, and upon the type of experiment. In many cases there seems to be undue simplification. If the weight loss of mixtures of sodium carbonate and silica in the ratios Na/Si = 8, 4 or 2 is determined up to 912°C., and the products analyzed it is said that the products are respectively, ortho-, pyro-, and meta-silicates.[31]

In the ternary system at temperatures below 1200°C. the high temperature modification α'–Ca_2SiO_4 is stabilized by concentrations of sodium carbonate greater than 20%, but above this temperature $CaNa_2SiO_4$ and free lime are formed.[32]

The decomposition of the mixed carbonates of sodium and calcium by silica is endothermic; the formation of the ternary sodium calcium silicates from the oxides is, however, exothermic.[33] The heats of reaction are calculated from the equilibrium carbon dioxide pressure in mixes of silica with sodium and calcium carbonates.[34]

The evolution of carbon dioxide from heated mixtures of β-quartz was used to determine the rate of the reaction, k, the maximum k values plotted as a function of temperature and the experimental initial temperature of the reaction determined.[35] (see section on Kinetics).

A study of the reaction between feldspar and sodium carbonate at 800–900°C. indicates the formation of $3Na_2O,SiO_2$ (II) with complete decomposition from a 16:1 molar ratio of carbonate and feldspar. It is suggested that the mechanism involves the decomposition of the carbonate to the oxide, which reacts to form (II), the other product being $K_2O,Al_2O_3,2SiO_2,4Na_2O$.[36]

Another investigation with pure sodium carbonate and purified quartz, which were heated together in various proportions under reduced pressures, shows that appreciable pressures were developed at 348°, 375° and 395°C. for 1:1, 2:1 and 1:4 mixtures. The pressure–temperature curves for these mixtures were recorded. The ratio of silica to sodium carbonate has no regular effect on the decomposition, although the 1:1 mix shows the least loss of carbon dioxide. Complete decomposition occurs with the 1:3 mix in 35 hr. at 650°C., in 15 hr. at 700°C., in 1·5 hr. at 800°C. and in 14 min. at 820°C. At the fusion temperature (825°C.) the reaction is very rapid; incipient sintering takes place at about 700°C. The residual mass after complete reaction is distinctly granular; the grains are similar to the original quartz particles and translucent; the compound seems to form an envelope about each quartz particle and slowly penetrates it.[38]

The reactions between sodium carbonate, barium carbonate and powdered quartz in the solid state have been partly investigated below the melting point. Mixtures of quartz and barium carbonate heated in a stream of carbon dioxide begin to evolve carbon dioxide noticeably at 700°C., but the addition of sodium carbonate lowers this temperature to 400°C. For isothermal mixtures of $BaCO_3$-SiO_2-Na_2CO_3 the amount of carbon dioxide evolved is proportional to log (duration of heating).[39]

The corrosion of glass BK7 (SiO_2 69, B_2O_3 11, K_2O 8, Na_2O 9, BaO 2 and Al_2O_3 0·5%) has been studied between 50 and 100°C. by the shift of the interference figures of the glass surface. With sodium carbonate solutions (2 N. to $1{\cdot}25 \times 10^{-6}$ N.) the amount of corrosion is proportional to the time of treatment and the velocity to the logarithm of soda concentration.[40]

The resistance of Na_2O-CaO-SiO_2 glass to soda decreases with increase of lime and decrease of silica. Detailed performance for various component concentrations is known. With a constant Na_2O content the resistance to soda increases with increase in the ratio Na_2O/CaO, and at a constant CaO content with decrease in that ratio.

The optimum composition of glass with respect to resistance to both soda and water is Na_2O 15, CaO 10 and SiO_2 75%.[41]

Data are available for the resistance of fused quartz as an industrial chemical material to sodium carbonate and other solutions.[42]

Measurements at 500°C. and 500 bars show that the solubility of quartz in alkaline solution is much greater than in water; in sodium carbonate it is proportional to concentration in the range 0·025 to 0·1 N., the solubility increasing in the order Li < Na < K.[43]

Sodium silicofluoride, Na_2SiF_6, a by-product from the fertilizer industry, may be continuously processed as a slurry by treating with sodium carbonate to give a mixture of hydrated silica and crystalline sodium fluoride; caustic soda is added to this in a second reactor; sodium fluoride crystals and sodium silicate solutions are recovered.[44]

Reactions of Cyanides with Sodium Carbonate.

The influence of changes of pressure and temperature on the absorption of hydrogen cyanide by sodium carbonate has been investigated. The optimum temperature for absorption is about 300°C. if the pressure is maintained at 230 mm., but if the pressure rises to 1 atm. the amount absorbed is much reduced. It is practicable to decompose impure sodium cyanide and to obtain a high-grade product in a closed cycle at low temperatures.[45]

The complex cyanide $CoZn(CN)_4$ reacts with 10% sodium carbonate solution to give zinc carbonate, $Co(CN)_2$ and $Na_4Co(CN)_6$. In boiling solution the carbonate converts $NiFe(CN)_5NO$ to $Fe(OH)_3$ and $Ni(CN_4)^{2-}$, but in the cold nickel carbonate and $Na_2Fe(CN)_5NO$ result.[46]

The Reduction of Sodium Carbonate.

The reaction $Na_2CO_3 + 2C \rightarrow 2Na + 3CO$ proceeds to the right at temperatures above 800°C.; it is reversed when the reaction products are cooled slowly in a miniature gas producer. With untreated Acheson graphite and dry air at 900°C., contact time 2 sec., the exit gases contained 6·8% of carbon monoxide, but when the graphite included 1% of sodium carbonate they contained 33% of carbon monoxide. As little as 0·1% of carbonate produces similar results. The carbonate is said to be decomposed in the high temperatures of the lower part of the producer, regenerated in the upper part, deposited on the fresh graphite, and so recycled. Foundry coke requires a higher percentage (5%) of carbonate, since it combines with the ash. Coke so treated gives a richer gas at 880°C. than the untreated coke does at 1090°C.[47]

The above reaction, which is very rapid above 900°C., follows the course:

$$\text{(i)}\ Na_2CO_3 + C \rightarrow 3CO + 2Na;$$
$$\text{(ii)}\ Na + CO_2 \rightarrow Na_2O + CO;$$
$$\text{(iii)}\ Na_2O + CO_2 \rightarrow Na_2CO_3.$$

The net effect is to increase the vapour pressure of carbon to 10^{15} times its actual value. The use of coke impregnated with soda in the gas producer is discussed under 'Utilization'.[48]

The reduction of sodium carbonate by carbon at 1050–1200°C. is employed in a patented process for the production of acetylene; the gaseous mixture of carbon monoxide and sodium from the reaction $Na_2CO_3 + 2O \rightarrow 2Na + 3CO$ is passed into contact with a mass of steel balls maintained at 625–780°C. which then become coated with a hard layer of sodium carbide, Na_2C_2, and sodium carbonate. The balls are treated with steam to convert the carbide into acetylene and then with carbon dioxide to recover the sodium carbonate.[49]

The Du Pont Cyanide Process.

The reaction $Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO$ is carried out by heating a mixture of soda ash, coke and a catalyst to approximately 975°C. in gas-fired retorts while nitrogen is passed through at atmospheric pressure. The best catalyst is finely divided iron, which gives a conversion of 70% in 4 hr., compared with 45% in 7 hr. with no catalyst. Increase in nitrogen pressure is without effect; indeed pure nitrogen is unnecessary since producer gas gives the same results if not more than 6% of carbon dioxide is present. The cyanized charge must not be permitted to cool in the presence of producer gas. The 'black liquor' from pulp manufacture on evaporation and heating provides a porous mass of 60–65% soda ash and 40–35% carbon.[50]

The reversibility of the reaction has been examined by passing carbon monoxide over a known mass of sodium cyanide, and nitrogen over soda ash and carbon, the equilibrium being approached from both sides. Consistent results can be obtained at 900°C.; below this temperature the reaction is too slow, and above, the volatility of the cyanide interferes. The relation

$$\log_{10}\{[X^2/(1-X)][(1-P)^3/P]\pi^2\} = \alpha + \beta/T$$

agrees within 1% with the experimental data over a wide range of conditions. X is the proportion of sodium in liquid phases combined as sodium cyanide (the yield of sodium cyanide), P is the partial pressure of nitrogen, and $\alpha = 23{\cdot}91$ and $\beta = -31{,}180$ are constants. π is the total pressure of nitrogen and carbon monoxide.[51]

Reactions with Titanium, Zirconium, Tungsten, etc. and their Compounds.

When titanium metal is heated in a fused salt bath, e.g. KCl 47, Na_2CO_3 47, LiCl 6%, a thin protective film, purple to black in colour is formed; it can be removed by sodium hydride treatment and contains titanium dioxide and lithium titanate.[52]

Zirconium ores (baddeleyite, ZrO_2; zircon, $ZrSiO_4$) may be sintered with excess soda ash, the product leached, and the water-insoluble portion dissolved in sulphuric acid and heated to yield commercially pure $Zr(SO_4)_2$, Na_2SO_4,H_2O and $ZrOSO_4$, $0{\cdot}75Na_2SO_4,H_2O$, depending on the sulphuric acid concentration.[53]

The waste after treating tungsten–titanium–cobalt alloys for tungsten may be fused with soda and potassium nitrate to form soluble tungstate and titanate, and insoluble cobaltocobaltic oxide, when separation is achieved by leaching with hydrochloric acid.[54]

Reaction with Nitrogen Oxides.

High-temperature drying seems to reduce the activity of sodium carbonate. Liquid N_2O_4 reacts with carbonate dried at 250°C. more rapidly than with the 600°C. product. At 250°C. the percentages converted into nitrate were: after 19hr., 49% and after 24hr., 64%; into nitrite 10% and 12·3%, respectively. At 600°C. after 19hr. there was 10·2% nitrate and 0·0% nitrite, after 24hr. 14·6% nitrate, 0·0% nitrite.[55]

The absorption of the gases in sodium carbonate solution has been explored.[56]

Reactions with Phosphates.

The formation of soluble phosphates from calcined phosphate rock is favoured by high excesses and high concentrations of sodium carbonate, and by low temperature. Grinding during the reaction is beneficial.[57] Aluminium phosphate is converted into alkali metal aluminate and alkaline-earth metal phosphate by calcining with chalk and soda proportioned to supply two moles of alkaline-earth oxide and one of alkali oxide for each mole of phosphorus pentoxide present in the mixture, and an additional mole of alkali oxide for each mole of alumina. The product can then be leached with water.[58]

The mixture of sodium carbonate and calcium phosphate is initially practically insoluble in ammonium citrate solution, but the solubility steadily increases as a result of the reaction $Ca_3P_2O_8 + Na_2CO_3 \rightarrow 2NaCaPO_4 + CaO + CO_2$.

Trisodium phosphate is prepared from sodium carbonate in two stages. Phosphoric acid is added to the carbonate to form Na_2HPO_4, carbon dioxide being released. The solution is filtered and diluted, and the requisite amount of aqueous sodium hydroxide is added; the solution is then heated, filtered hot, and crystallized. Caking may be prevented by the formation of double salts.[59]

Apatite and soda react on fusion according to the equation:

$$3Ca_2(PO_4)_2.CaF_2 + 12Na_2CO_3 \rightleftharpoons 6Na_2PO_4 + 6NaF + 12CaO + 12CO_2;$$

more than half the apatite is decomposed.[60]

Reaction with Niobium Pentoxide.

When one mole of niobium pentoxide is heated with 3 moles of sodium carbonate at temperatures greater than 700°C., the orthoniobate, Na_3NbO_4, is formed; it is slightly soluble in water and is thus separable from the insoluble metaniobate, $NaNbO_3$, which is formed at the same time. The identity of both compounds has been established by X-ray examination.[61] An extension of this work indicates that there is no reaction below the melting point of sodium carbonate either at atmospheric pressure or *in vacuo*. In the 3:1 mixture it is possible that a little pyroniobate, $Na_4Nb_2O_7$, is present and in the 5:1 mixture a little Na_2NbO_5. The metaniobate is a stable substance, not an intermediary; it can be heated with sodium carbonate at 875°C. for 1 hr. *in vacuo* without change.[62]

Reactions with Compounds of Arsenic, Antimony and Bismuth.

When stibnite is heated in a slow stream of hydrogen at about 500°C. for 30 min. and then at 550°C., the residual metal contains about 99% of antimony; over 85% of the sulphur can be converted into sodium sulphite by the reactions $Sb_2S_3 + 3H_2 \rightarrow 2Sb + 3H_2S$; $3H_2S + 3Na_2CO_3 \rightarrow 3Na_2S + CO_2 + H_2O$, with anhydrous carbonate.[63]

The additions of arsenious oxide to solutions of sodium carbonate increases the amount of hydrogen sulphide which can be taken up. A carbonate solution containing 0·2% of As_2O_3 was used five times for the absorption of hydrogen sulphide after regeneration but no sulphur formation was detected.[64]

Polonium carried down with bismuth hydroxide in a sodium carbonate solution is distributed between the solid and liquid phases as a function of the number of moles of bismuth and the number of moles of carbonate in a fixed volume of the solution.[65]

Reactions with Sulphur and Sulphur Compounds.

Sodium carbonate attacks both colloidal and rhombic sulphur but not so vigorously as caustic soda.[66] Dilute aqueous carbonate (1·5 → 3·0 N.) dissolves some 0·10 wt.-% of molybdenum sulphide MoS_2 at low temperature and some 0·40% at 90°C., both over 0·5 to 6 hr.[67]

Sodium carbonate may be prepared from sodium sulphate by reduction with carbon monoxide in the presence of water vapour. The mixed gases may be passed over powdered sulphate in a boat; the reaction starts slowly at 720°C. but becomes very rapid at 750°C., when the charge melts. If ferric oxide is used as a catalyst (derived from ferric nitrate *in situ*) the powdered charge may be replaced by pellets in a column between perforated plates. At 660°C. with $p_{H_2O} = 0{\cdot}3$ atm. there is 96–7% reduction in 4 hr. with a yield of 85–92% of Na_2CO_3.[68] The reaction was followed with producer gas and mixed catalysts. With 7% carbon monoxide (17% in excess of theoretical requirements) only 15·6% conversion was obtained; with 9·2% it was 70% complete and with 14·6% (158% in excess) reduction reached 93·8%, corresponding to 88·5% of Na_2CO_3.[69] If the air was saturated with water (semi-water gas) before entering the gas generator 97·2% reduction and 92·7% of Na_2CO_3 were obtained at 630°C. and $p_{H_2O} = 0{\cdot}35$ atm.[70]

Reactions with Chromium Compounds.

The action of sodium carbonate on chrome alum solutions is of importance in the leather industry. If freshly prepared solutions are allowed to stand at constant temperature in diffused light, the amount of carbonate required to start precipitation rises to a maximum varying directly with temperature and concentration over periods from a few hours to days; it then slowly falls to a minimum in weeks or months. It seems that chromium sulphate hydrolyzes, the chromic hydroxide being peptized by the sulphate. Further hydrolysis increases the ionization and conductivity and lessens the peptization of the hydroxide. It is the first reaction which results in an increase of carbonate required to produce precipitation; the second leads it to a maximum and subsequent decrease.[71-73]

The oxidative fusion of chromite with sodium carbonate can be aided by the addition of 40% ferric oxide instead of the usual lime. A better leaching of the chromate appears possible and the ferric oxide can be recycled.[74]

The optimal conditions and rate of the reaction $2Na_2CrO_4 + 2CO_2 + H_2O \rightleftharpoons Na_2Cr_2O_7 + NaHCO_3$ have been studied in both directions. The chromate solution was treated with carbon dioxide under moderate pressure in an autoclave at 25°C.; after 12hr. at 10atm., 48·35% conversion was obtained, and at 5 atm., 23%. By shaking for 12hr. at 25°C. and 10atm. there was 81% conversion. At atmospheric pressure the rate of chromate conversion is slow enough to make the removal of the bicarbonate by vacuum filtration practical for the industrial preparation of dichromate.[75] If the latter procedure is carried out at low temperatures and high pressures (15°C. and 8atm.) the yield is 93%.[48,77]

A 2:1 mixture of calcium chromate and sodium carbonate when heated loses carbon dioxide and forms a basic chromate, $4Na_2O,8CaO,8CrO_3$. On heating this further decomposes to form $4Na_2O,8CaO,6CrO_3,Cr_2O_3$, then $3Na_2O,6CaO,4CrO_3,Cr_2O_3$ and $5Na_2O,10CaO,6CrO_3,2Cr_2O_3$.

The characteristic decomposition pressures of these chromates indicate heats of decomposition of 14·9, 43·6, 24·4 and 37·4g.-cal./mole respectively.[78]

Reactions with Compounds of Chlorine, Manganese, Iron and Nickel.

The main reaction of solid sodium carbonate with chlorine proceeds thus: $2Na_2CO_3 + 2Cl_2 \rightarrow 4NaCl + 2CO_2 + O_2$. If the carbonate is formed by heating bicarbonate at 350°C. 86% is changed at 300°C. in 15min., but if prepared at 500°C. only 80% undergoes the change at 600°C. If the temperature of reaction is below 450°C., sodium perchlorate is also formed.[79]

Provided no excess of sodium chloride is present, a solution of 200–300g. Na_2CO_3/l. is best chlorinated at 60°C. During the process sodium bicarbonate and hypochlorite are formed. When all the carbonate has reacted chlorination of the bicarbonate begins, the hypochlorite forms chlorate and the eventual yield is 97% $NaClO_3$; it is not increased by prolonged chlorination.[80]

Sodium carbonate solutions containing sodium sulphide may be purified by boiling with excess manganese dioxide added in small portions without stirring. The reaction is $2Na_2S + 4MnO_2 + H_2O \rightarrow 2NaOH + Na_2S_2O_3 + 4MnO$. If too much dioxide is added the thiosulphate may be oxidized to sulphate.[81]

At 800°C. sodium carbonate reacts with iron pyrites, FeS_2, to yield Na_2S. The reaction is slower at lower temperatures down to 500°C. and is not improved by raising the temperature to 1000°C. In the absence of lime, there is a 50% yield; up to 1·75g. CaO per g. of FeS_2 the lime has no effect, but at 2g./g. the yield rises to 76·5%. The lime may perhaps keep the mass porous, or may inhibit the formation of a double sulphide of sodium and calcium. In the absence of air, sodium sulphate is not a product.[82]

The use of sodium carbonate in the desulphurization of iron is discussed more fully in the section on Utilization. A laboratory research indicates that the fundamental reactions $FeS + MO \rightarrow MS + FeO$ and $FeO + C \rightarrow Fe + CO$ can take place below the melting point of the reactants. The behaviour of a number of oxides (lime, strontia, baryta, manganese oxide, magnesia, etc.) was investigated, and it was found that the carbonates (including sodium carbonate) react with ferrous sulphide and charcoal at lower temperatures than do the oxides, and at temperatures lower than the dissociation temperatures of the carbonates in the presence of charcoal.[83]

A method of purification of nickel sulphate solutions in the preparation of a hydrogenation catalyst depends on the use of sodium carbonate according to the equation

$$CaSO_4 + 2Na_2CO_3 + 2H_2O + FeSO_4 \rightarrow 2Na_2SO_4 + 2CO_2 + Fe(OH)_3 + CuOH.$$

The catalyst is heated at 85–95°C. with a solution of copper sulphate and sodium carbonate; the brownish-red precipitate contains iron, copper, and aluminium as hydroxides with which the phosphorus and arsenic content forms water-insoluble compounds. The nickel sulphate reacts to form the carbonate only after all impurities have been precipitated.[84]

Nickel carbonate precipitation is effected by adding to a solution of nickel chloride (47 g. Ni/l.) a 10% excess of aqueous sodium carbonate (180 g./l.) between 0° and 50°C. The precipitate, dried at 100°C., has a molar ratio $NiCO_3{:}Ni(OH)_2$ of 1–1·6. The ratio value can be predetermined by appropriate choice of the temperature of precipitation; the greater the relative concentration of nickel carbonate, the more crystalline the compound.[85]

The film formed on iron by 0·1 N. solutions of sodium carbonate and other alkaline salts in the presence of air but without the air-formed film has been removed and examined by electron diffraction; it consists mainly of a cubic oxide (magnetite, γ-ferric oxide, or an intermediate compound).[86]

The reaction between ferric salts and alkalies is complicated. A study was made at 15°C. of the ferric sulphate-alkali system beginning with a 14·5% aqueous ferric sulphate solution. The composition of the precipitate is not constant; it is free from sulphate only when an excess of alkali is added. The composition also depends on the pH of the mother liquor; with $pH > 5{\cdot}6$ basic sulphates may exist, varying from $Fe_2O_3,3SO_3$, aq. to $4Fe_2O_3$, SO_3, aq. With sodium carbonate, if the ratio of $Fe{:}\frac{1}{2}Na_2CO_3$ is 1:3 there is no precipitate, but a reddish colloidal solution is formed; if it is as low as 1:8·4 there are only faint traces of reaction.[87,88]

Causticization by Lime.

The process depends on the respective solubilities of calcium hydroxide and calcium carbonate and is adversely affected by the presence of sodium sulphide when calcium sulphide enters into the reaction. OH^- ions formed by hydrolysis and the S^{2-} ions present both diminish the yield, more so at high temperatures because of the tendency to polysulphide formation.[89]

Commercial wheat or potato starch (0·01% on liquor volume) or peeled potatoes may be incorporated in the process; the speed of precipitation of the chalk sludge is five times that without additions, or twice that with the addition of powdered limestone. The use of the starch is effective up to a concentration of 100 g. of NaOH per l. of liquor.[90]

Causticization by Ferric Oxide.

This is the Löwig process, which was largely investigated by Russian and by Japanese workers in the years between the wars;[93] it depends upon the formation of sodium ferrite by fusion of ferric oxide with soda, and its subsequent decomposition by water.[76,91,92,94,95] The ferrite is formed at 75°C. in 96–97% yield by heating 1 part of carbonate with 1·8 parts of ferric oxide, and more rapidly at higher temperatures. It is stable to water below 35°C., but decomposes rapidly at 40–60°C. and completely at 70°C.[95] The work is considered at somewhat greater length in the Section on Utilization, but the data below are of interest here.

The dissociation pressure of sodium carbonate in the presence of ferric oxide is represented by the equation:

$$\log p = -7409{\cdot}0T^{-1} + 1{\cdot}75 \log T - 0{\cdot}001720T + 6{\cdot}0808$$

giving

$$\Delta H = 33{,}896 + 3{\cdot}477T - 0{\cdot}007869T^{2}$$

with $\Delta H_{298\cdot1}$ = 34,574 g.-cal.[76] At 760 mm. the dissociation temperature of sodium carbonate in the presence of ferric oxide is 855–856°C. The heat of solution in hydrochloric acid of the ignited product enables the heat of formation of sodium ferrite to be calculated; we have

$$Fe_2O_3(s) + Na_2O(s) = Na_2O,Fe_2O_3(s) \quad \Delta H = 42{,}695{\cdot}6 \pm 35{\cdot}2 \text{ g.-cal.}$$

and[76,96]

$$Na_2CO_3(s) + Fe_2O_3(s) = Na_2O,Fe_2O_3(s) + CO_2(s) \quad \Delta H = 34{,}357 \text{ g.-cal.}$$

Reactions of Sodium Bicarbonate

Thermal Decomposition.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

(at 100°, 115° and 120°C.).(See also Physical and Thermodynamic Properties). The ratio H_2O/CO_2 remains unity except at the moment of disappearance of $NaHCO_3$, when it rises to 1·8 and falls rapidly to 1. At 101°C. the dissociation pressure reaches 1 atm. but even at 120°C. the rate of dissociation is hardly noticeable. Only above 140°C. is the rate fast enough for commercial use. Pure bicarbonate at a pressure of 0·01 mm. (over phosphorus pentoxide) gradually gives off carbon dioxide; at 18°C. in a 30 ml. container the pressure rose to 1 mm. after 20 days.[97] The exposure of sodium bicarbonate to 120–170 kV. electrons in a current of 0·005 milliamp. produces complete decomposition to the carbonate in about 30 min.[98] The decomposition, which (as above) is almost complete in 3 hr. at 100°C., is retarded by an admixture of 3% saccharin so that only 2·2% has decomposed in 10 hr.[99]

The effect of temperature, rate of heating, grain size and pressure on the reaction has been examined. Some 8–16 g. bicarbonate were placed in a combustion tube with a thermoelement inside a constant temperature furnace. At atmospheric pressure the evolution of carbon dioxide and water takes place at a constant temperature (124°C.) which is independent of the amount of material. This temperature increases with grain size and with increasing temperature, the decomposition and equilibrium temperatures are different but approach each other with increasing external pressure.[100]

The reaction is partly reversed by the moisture and carbon dioxide of the air, soda being converted into bicarbonate. Tables are available giving the water and bicarbonate content of soda ash for various periods and climatic conditions.[101] The decomposition on heating the solid may be prevented by the addition of non-surface-active salts such as sodium formate or the free carboxylic acids. The bicarbonate heated alone for 2, 3 and 4 hr. at 140°C. gives products with 75, 94 and 99% Na_2CO_3 respectively; of the substances cited it may be noted that under the same conditions the corresponding percentages are: benzyl alcohol 47, 57, 66; 3% sodium formate 15, 23, 26; sodium citrate 20·4, 32·2 and 42·4%.

Reactions with Mercurous and Mercuric Chlorides.

Mercurous chloride is incompatible with sodium bicarbonate since the reaction $Hg_2Cl_2 + 2NaHCO_3 \rightarrow HgCl_2 + Hg + Na_2CO_3 + CO_2 + H_2O$ occurs.[102] Mercuric chloride gives a red precipitate of $HgCl_2,2HgO$. A period of induction precedes the precipitation and is inversely proportional to the concentration of each reactant. It is diminished by a rise in temperature (5 sec./10°C.), or by the addition of tartrates, or of methyl, ethyl or *iso*propyl alcohol. It is increased by propyl alcohol, glycerol and certain salts. It is presumed that a number of intermediate reactions are responsible for the delay, the feeble ionization of mercuric chloride in aqueous solution contributing. The shortening of the induction period with methyl and ethyl alcohol is thus due to the increase in ionization.[103]

buting. The shortening of the induction period with methyl and ethyl alcohols is thus due to the increase in ionization.[103]

In a later investigation equal volumes of 0·01 M. $NaHCO_3$ and 0·01 M. $HgCl_2$ were mixed at 18°C. At alkaline salt concentrations less than 0·05 M. there is no precipitate, whatever the amount of mercuric chloride solution. Light seems to have no effect. At higher concentrations the nature of the deposit depends on the concentration ratios. The principal factor affecting the composition and weight of precipitate is the pH, as appears in Table XXVIII.

TABLE XXVIII.- EFFECT OF pH ON REACTION OF SODIUM BICARBONATE WITH MERCURIC CHLORIDE

pH	Product
6–7	$HgCl_2,2HgO$
7·1–8·5	Series of solid solutions of $HgCl_2,2HgO$ and HgO
8·5–8·7	$HgCl_2,4HgO$
8·7–10·8	Mixtures of $HgCl_2,4HgO$ with HgO
> 10·8	HgO

The supposed salt $HgCl_2,3HgO$ is a solid solution of $HgCl_2,2H_2O$ and HgO, confirmed by *X*-ray data.[104]

Miscellaneous Reactions.

Solid hydrocarbonate and alcoholic phosphoric acid yield a very hygroscopic substance with the empirical composition Na_2CO_3,H_3PO_4; this is decomposed readily by water giving carbon dioxide.[105]

Sodium bicarbonate reacts with nascent chlorous acid ($H_2O_2 + ClO_2$ solution) at about 2°C. Standing for five hours gives approximately a 94–98% yield of sodium chlorite.[106]

The reduction of the oxides of iron (below 900°C.) and of copper (below 700°C.) may be effected by heating them with small quantities of bicarbonate in a rotary furnace in an atmosphere of carbon monoxide or hydrogen.[107]

The conversion of bicarbonate in aqueous solution to carbonate on heating is catalyzed by the addition of small amounts of salts of metals such as iron, which form basic carbonates or whose carbonates or bicarbonates split readily into oxide and carbon dioxide. Thus sodium bicarbonate in solution when heated alone for 1½ hr. gives a yield of 66·2% of Na_2CO_3; when heated for the same time with a trifling addition of ferric chloride the yield is 85%.[108]

When sodium bicarbonate and metallic sodium in separate boats are sealed under vacuum in a small tube and kept at room temperature, pressure determinations show the evolution of gas, the normal equilibrium being displaced by the sodium which reacts with the water vapour to form hydrogen. The rate of pressure rise was initially several mm. per day, but this fell and a maximum value of 35 mm. was reached after 45 days. After 2 to 3 years the pressure had decreased to 3 mm. perhaps owing to absorption of carbon dioxide by sodium hydroxide and of hydrogen by sodium to give the hydride.[110] The faint reddening of phenolphthalein by bicarbonate has been variously attributed to traces of soda carried over in the process of manufacture and to the carbonate produced by the reaction $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$. Samples examined after long periods seem to show a constant initial alkalinity, an observation which supports the first suggestion, but the disproportional reaction certainly takes place.[111]

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The absorption coefficients of carbon dioxide in concentrated sodium carbonate-bicarbonate solutions show complex variations: the density, viscosity, surface tension and pH for these solutions (upwards of 230 g. Na_2CO_3/l.) have been studied. Surface tension values were erratic and the variations in absorption coefficients seem to run parallel with these.[112]

The Sodium Percarbonates.

A revision of the contradictory work on these compounds has been carried out. The monobasic sodium monopercarbonate, $NaHCO_4$, is confirmed, together with $Na_2C_2O_6$ and other alkali salts. The supposed isomeric Na_2CO_4, $1{\cdot}5H_2O$ and $Na_2CO_3,H_2O_2,0{\cdot}5H_2O$ were shown to be identical. $Na_2C_2O_6,H_2O_2$ and $Na_2C_2O_6,C_2H_5OH$ were not confirmed. The gradual addition of excess solid bicarbonate to 10 or 30% hydrogen peroxide gives a solid free from active oxygen below 0°C. or even at room temperature. If however the solid is set aside in contact with the solution for some four hours, Tanatar's salt $Na_2CO_4,\frac{1}{2}H_2O_2,H_2O$ is formed.[113] See however below.[115] Stable perhydrates of sodium carbonate are said to be prepared by removing deleterious impurities (particularly iron) from the carbonate solution, by use of magnesium or calcium carbonates as 'collectors' and by subsequent treatment with hydrogen peroxide in the presence of pre-formed crystals of $Na_2CO_3,1{\cdot}5H_2O_2$. A little sodium silicate solution is added as a stabilizer. The product contains 15•23% of active oxygen corresponding closely to the formula; there appears to be little loss on storage even for a month at 50°C.[114]

In a fairly recent paper the thermal characteristics of dehydration with hydrogen peroxide have been examined by heating the compound $Na_2CO_3,H_2O;$ $1{\cdot}5H_2O_2$; this shows an endothermal effect at 155°C. corresponding to loss of water, and an exothermal at 120°C. corresponding to the decomposition of crystalline hydrogen peroxide. $Na_2CO_3,H_2O,2H_2O_2$ behaves similarly. Na_2CO_3, $1{\cdot}5H_2O_2$ and $Na_2CO_3,2H_2O_2$ can thus be prepared by heating the hydrated compounds.[115] Active oxygen determinations support the view that sodium percarbonate is a loose addition compound of sodium carbonate and hydrogen peroxide.[116]

Radio-Chemistry.

The colouration of sodium carbonate by β- and γ- rays from radium chloride at a distance of 1 to several cm. is discussed and compared with the changes in other related materials. It depends on changes in structure of atoms and ions. It has been stated that sodium carbonate powder is not coloured by radium irradiation unless it is compressed, when it becomes blue or purple.[117]

The preparation of sodium 'radiocarbonate' ($Na_2{}^{14}CO_3$) may be carried out by treatment of 35 mg. of barium 'radiocarbonate' with excess (35 mg. in 0•5 ml. of water) of dilute perchloric acid. The $^{14}CO_2$ evolved is absorbed in aqueous sodium hydroxide with the necessary precautions.[118]

Exchange Reactions.

The oxygen exchange in powdered sodium carbonate with gases and aqueous solutions has been followed with the isotope ^{18}O. There are apparently two types of reactions: there is atomic exchange during interaction with gases at elevated temperatures (not exceeding the threshold of ionization), and exchange in aqueous medium, where the carbonate interacts with the ions of the solution. Sodium carbonate was prepared with a ratio $^{18}O/^{16}O$ of from 0•35 to 1%, and gaseous exchange was effected with oxygen and carbon dioxide from cylinders; the magnitude of the exchange was determined by mass spectrometry using the 44 and 46 peaks ($C^{16}O_2$ and $C^{16}O^{18}O$) from carbon dioxide derived from the initial enriched carbonate. The gaseous exchange, unlike ionic exchange, is not dependent on the presence of water vapour. With sodium carbonate the exchange with gaseous oxygen proceeds more easily than with carbon dioxide and apparently involves the general breaking up of the oxygen bond in the molecule, and the intense diffusion of the gas into the carbonate lattice but not with loss of carbon dioxide and formation of sodium oxide. The thermal stability of the carbon-to-oxygen bond decreases in the carbonates in the series barium, sodium, calcium to magnesium.[119] The double-exchange tendency of ^{18}O and of deuterium in the recrystallization of $Na_2CO_3,10H_2O$ from waters containing various amounts of ^{18}O is in favour of the crystals for ^{18}O and against them for deuterium. The hydrate was obtained by recrystallizing the anhydrous salt from enriched water. The observation was confirmed by a determination of the isotopic content of the residual mother liquor, which was found to be low in ^{18}O and high in deuterium. In contact with water, enriched sodium carbonate (^{18}O) suffered 71% exchange in 212 days, whereas calcium carbonate showed not more than 1%.[120] In the exchange of free carbonate or bicarbonate ion labelled with ^{14}C and complexed CO_3^{--} in solutions of carbonatopentammine cobaltic nitrate, $[Co(NH_3)_5CO_3](NO_3)$, the rate was measured as a function of reactant concentrations, of pH and of temperature. Exchange was postulated to occur by two concurrent processes, one of direct collision and the other of aquation (the displacement of a CO_3 group by H_2O). The primary step in the aquation of the complex is the addition of H^+ ion to form the bicarbonato-complex. It is not possible in this way to decide between the rupture of the Co–O bond and the C–O bond within the complex, although studies of the relation between ionic strength and exchange rate appear to favour the Co–O mode.[121] In a solution approximately 0•03 M. in carbonatotetrammine cobaltic nitrate $[Co(NH_3)_4CO_3]NO_3$ and 0•01 M. in sodium carbonate containing a small amount of ^{14}C, exchange occurred at 20°C. in the dark with a half-life of 7 hr. The reaction had first-order characteristics.[122]

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THE KINETICS OF REACTIONS INVOLVING SODIUM CARBONATE

The absorption of carbon dioxide by reactive or indifferent solutions has formed the basis of much research in gas-liquid kinetics. The experimentation is more difficult than would at first appear; this is borne out by the variation in the results obtained. For example there was uncertainty for some time as to whether the initial rate of absorption of the gas by dilute aqueous sodium carbonate was faster than with pure water. Thus in one investigation with a stirring rate of 400 r.p.m., the initial absorption rate per unit area (moles/sec./cm.^{2} $\times$ 10^{-9}) for 400 ml. of water, M. sodium hydroxide and M. sodium carbonate was respectively 94, 218 and 235,[1,2] while in another and later series of experiments at 192 r.p.m. for 100 ml. the rate was for water 133 and for 0•17 M. sodium carbonate, 170.[3] Further aspects of this problem sometimes produce irreconcilable results, and it was thought best to draw attention to some important and comprehensive work without attempting a definite exclusive summation.

Mechanism.

An apparatus has been devised for ensuring short gas–liquid contact periods of 0•2 to 0•005 sec. It is verified that equilibrium always exists at the liquid–gas interface and that solute molecules diffuse across the gas and liquid films. The absorption of carbon dioxide in aqueous sodium carbonate and caustic soda shows that the equilibrium at the interface is reached instantaneously ($<$ 0•005 sec.). The solute gas molecules diffuse from the interface into the interior as the reaction proceeds.[4] The 'stagnant film' theory has been criticized[5] and a continuously changing liquid phase is suggested; the mechanism of mass transfer may be based on turbulent and convectional diffusion with molecular diffusion playing only a secondary role.[6,7] In experiments based on this hypothesis the kinetics of the absorption reaction were studied; 98% carbon dioxide was led into a liquid phase of constant viscosity at six different stirring rates. The data were treated according to the equation $d\omega/d\tau = \{mC[1 - e^{-PHK}] + PH\}/\rho$, where $d\omega/d\tau$ is the rate of absorption, m is the stoicheiometric coefficient of the reaction, C is the concentration of the chemosorbent, P the partial pressure of the absorbed gas, H the solubility of the gas and ρ is a constant. At low turbulence an increase in concentration increases the rate of absorption but at high turbulences decreases it.[8] The kinetics of bubble absorption were explored with carbon dioxide and sodium carbonate and a simplified expression $d\omega/d\tau = HP(KC + 1)/\rho$ found to apply. The absorption of sulphur dioxide by carbonate is said to be 'not a physical process' but one controlled by the reaction $H_2O + SO_2 \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3$.[9] An attempt has been made to represent the absorption of a gas by a chemically reactive solution as a kinetic mechanism based on a process of two consecutive chain reactions, the kinetic constant of the first being much smaller than that of the second and of the order of the diffusivities of the reagents in the liquid film. In particular, the concentration a_i of the gas at the liquid–vapour interface depends on the concentration q_0 of the carbonate by a relation of the type $a_i = mq_0^n$. n is a parameter having the same mean exponential value as that to which the normal concentration of sodium is raised in the absorption of carbon dioxide in sodium carbonate solution.[10] This finds some support in another set of experiments where it is said that as a result of the practically instantaneous reaction $CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$, the velocity of absorption of carbon dioxide by hydroxide solutions depends both on the partial pressure of carbon dioxide in the gas and on the concentration of hydroxide. The process of absorption in a carbonate solution, resulting in the formation of bicarbonate, is accompanied by the relatively slow hydration of the gas. The initial carbon dioxide content of the gas varied from 2•4 to 80%, the rates of flow from 800 to 1700 ml./min., the total pressure being 740 mm. at 18–20°C., and the sodium carbonate concentration varied from 0•360 N. to 0•915 N. and bicarbonate from 0•015 N. to 0•560 N. The rate of absorption of carbon dioxide was shown to depend only on its own partial pressure, p, and to be independent of either the sodium carbonate concentration or the rate of flow of the gas; it was found to be given by the equation N(moles/m.^{2}/hr.) $= \beta Hk(p - p_e)$ where H is Henry's coefficient, k = partial coefficient of the rate of transfer across the liquid film, p_e = equilibrium pressure of carbon dioxide over the solution, and β = a chemical parameter which depends upon the rate constant of the chemical reaction, the effective thickness of the liquid film, and the diffusion coefficient of the dissolved molecules of the gas. If $p_e \ll p$, this simplifies to $N = \beta Hkp$.

Of the right hand factors β is determined by the rate of the chemical reaction; the fact that it is independent of the concentration indicates that this reaction is the hydration of carbon dioxide.[11,12]

A fairly exhaustive examination of the rate of absorption of carbon dioxide in a small tower with glass rings showed that with the various liquids used virtual saturation was reached at the bottom of the tower at 25°C. The overall absorption coefficient K_G is derived from the expression $K_G.a = (W/\theta)/V\Delta P$, where a is the interfacial area per unit of tower, W/θ is the amount absorbed in unit time, V is the volume of the section of the tower in which absorption takes place, ΔP is the mean driving force in pressure units, *i.e.* the difference between the partial pressure of the solute gas in the gas phase and in equilibrium with the main body of liquid at the given level.

K_G for water is approximately 0•128 to 0•188 and for sodium carbonate 0•05 to 0•10. No coefficient could be calculated for the bicarbonate, but the rate is considerably less for the dilute aqueous solution than for water. The tabulated results indicate that (i) the average overall coefficient is independent of the carbon dioxide concentration in the gas, (ii) fourfold increase in the gas rate has no effect on the coefficient, but (iii) increase in liquid rate has, very materially, (iv) a sixteen-fold variation in sodium carbonate concentration has no significant effect on the coefficient, (v) increase in temperature gives large increases in K (0•06 at 5°C. to 0•67 at 85°C.), and finally (vi) the coefficient for dilute caustic soda is much greater and, as other work has shown, a purely physical diffusion theory is not adequate but must be supplemented by considerations of the chemical reaction rate.[2]

Several. gas–liquid mixers have been devised for the exploration of this reaction. In addition to the short-period contact device described above,[4] various types of towers with baffles, rings and other fittings have been used. Investigators have emphasized that the speed of agitation has a minimum value for effective absorption,[13] and that at any given speed of the agitator the absorption of carbon dioxide is a complex phenomenon, influenced by many factors such as viscosity, surface tension, density and pH. When plotted against agitator power consumed, the average absorption coefficient is $K_G = CP^{0\cdot6}$, where C is a dimensional constant.[14] Observed complex variations in absorption coefficients have been attributed chiefly to variations in surface tension. At above 16% conversion solutions are saturated at 25°C. with bicarbonate.[15] With both carbonate and bicarbonate initially present, the solutions being 1 to 2 N. in Na^+, and temperatures varying from 25 to 63°C. in a wetted-wall absorption tower, the coefficient of absorption K_G was independent of $[Na^+]$, but decreased about 40% with increase in $[HCO_3^-]$ from 0•2 N. to 0•6 N. and increased two-fold with a 22°C. rise in temperature.[16]

From a 13•4% gas mixture, carbon dioxide was absorbed in 2•054 N. soda solution; the overall coefficient was 0•0405 g./hr./ml. of tower volume. With sodium sulphate (1•50 equiv./l.) present, the coefficient was 0•0236; with surface tension reduced from 77•8 to 49•3 dynes/cm. by soap, 0•0414, and to 33•2 by 0•024 g./l. of a lauryl sulphate detergent it was 0•0514.[17] The presence of other substances therefore has a pronounced effect. In an investigation of the absorption of carbon dioxide from air by carbonate and caustic soda–carbonate mixtures, many variables (liquid rate, gas rate, p_{CO_2}, packing size and height) were examined; good correlation was given by an empirical equation for the rate constant at different packing heights and it was found to be independent of gas rate and packing size, but slightly dependent on the mole fraction of carbon dioxide in the gas, and increased slightly with the normality of the solution up to 1•5 N., when it began to decrease. The conclusion was reached that reactions involving non-ions control the rate.[18] The accelerating effect of formalin on the velocity of absorption of carbon dioxide by carbonate solution was studied at 25°C., 98% carbon dioxide, gas velocity 100 ml./min., gas agitation 114 r.p.m., solution stirring 140 r.p.m. in 500 ml. of solution. In these conditions 11 ml. of formalin gave the maximum effect. The maximal absorption velocity is a decreasing linear function of the molar fraction of bicarbonate. The rate of increase when v ml. of formalin are added is $(A_v - A_0)/(A_{\text{max.}} - A_0)$, where A_v and $A_{\text{max.}}$ are respectively the absorption velocities when v ml. of formalin and the maximal-velocity-producing volume are added, A_0 being the rate with no formalin. The rate of increase is related to the concentration of the solution.[19]

The velocity of absorption of carbon dioxide by ammoniacal solutions is of course of considerable technical importance. Curves are available for 20°C. for a solution containing 0•04 M. ammonium carbonate in 100 g. of water and varying quantities of sodium bicarbonate. The velocity, expressed in ml. of gas absorbed in 1 sec. by unit surface, varies linearly from 50×10^{4} for 0•1 mole of sodium bicarbonate per 100 g. of water to 250×10^{-4} at zero bicarbonate.[20]

Many simple organic crystalloids increase the rate of absorption, changes in viscosity having very little effect. The chemical function of the additive plays an important part, the substances investigated including methyl and ethyl alcohols, aldehydes, glycol, glycerol and sugars. Acetaldehyde at a concentration of 0•0037 g. per 100 ml. of solution increases the rate relatively from 43•4 (no additive) to 50 and at 0•3 g./100 ml. the relative rate is 130.[21,22] Some lyophilic colloids lower the rate, at first very rapidly but at $\frac{1}{8}$% concentration the velocity remains constant at about two-thirds the original.[23]

The absorption of some other gases by aqueous sodium carbonate has been explored.

Sulphur Dioxide.

In the tower absorption on a laboratory scale with a 3–7% gas it seemed that the reactions (i) $2Na_2CO_3 + SO_2 + H_2O \rightarrow 2NaHCO_3 + Na_2SO_3$ and (ii) $2NaHCO_3 + SO_2 \rightarrow Na_2SO_3 + H_2O + CO_2$ begin almost simultaneously, (i) being completed before (ii). When (i) and (ii) are finished, (iii) $Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3$ sets in. The maximum concentration of bicarbonate reached is 9–11%; of sodium sulphite 12–14%, but a temperature of not less than 60°C. must be maintained to prevent precipitation of bicarbonate and bisulphite.

The reaction is of importance in the manufacture of sulphite cooking liquor. It is essentially a three-stage reaction, as above; in the first stages the gas-film resistance controls the sulphur dioxide absorption. In an experimental tower at a liquid rate of 3130 lb./hr. ft.^{2}, the absorption coefficient K_G varied from 9 lb.-mol./hr. ft.^{3}atm. at a gas rate of 100 lb./hr. ft.^{2} to 20 at a rate of 500. In the second stage sulphite or bicarbonate is converted to bisulphite, as above. The overall coefficient is about 4 lb.-mol./hr. ft.^{3}atm. for a liquor rate of 1500 lb./hr. ft.^{2} and a concentration range of 0•5–1•0 M. The final stage is the build-up of free sulphur dioxide.[24]

Bromine.

The absorption with up to 2–3% of bromine in the gas phase is determined by the rate of diffusion through the gas film and is given by $g = K_r F t P_m$, where K_r is the coefficient of absorption rate determined by the gas film in kg./m.^{2}/hr./atm., F the absorption surface in square metres, t the time in hours, and P_m the partial pressure of bromine. The gas was passed over the surface of the stirred solution. With the higher percentages of bromine, the results may be well expressed by $g = KFt(rC + P)_m$ where r is the coefficient and C the molar concentration of absorbing solution.[25]

Hydrogen Sulphide.

This again is a heterogeneous diffusion process accompanied by a fast chemical reaction in the liquid phase. The rate of absorption varies with the concentration, c, of absorbent and with the partial pressure, p, of hydrogen sulphide. The driving force of the process is the sum of the partial pressure of hydrogen sulphide and the 'pressure equivalent' of the chemical capacity of the absorbent in the solution. In the region of partial pressures from 0•02 to 0•70 atm. the rate is very sensitive to changes in c; changes in p affect the rate to a lesser degree. The resistance of the diffusion of the liquid boundary layer is 94•3% of the total diffusion resistance. The rate of absorption can be approximately represented by $dG/dF = k(rc + p)t$ where G is the amount of substance absorbed, t = time, F = surface of contact between the two phases, r and k being coefficients. It is noteworthy that in the region of low partial pressures (below 0•02 atm.) a sharp change in the mechanism of absorption is observed. The liquid boundary layer seems to stop controlling the process, and the rate of absorption is not affected by changes in c, but increases sharply with increase in p and is therefore given approximately by $dG/dF = kpt$.[26]

Oxidation by Air of Sodium Sulphite Solutions in Presence of Sodium Carbonate.

The oxidation velocity is independent of the sulphite concentration but is a linear function of the carbonate concentration if > 0•02 N. Change of temperature has a negligible effect. Calculations are available showing the solution velocity of oxygen in carbonate solutions of various concentrations.[27]

In another investigation the solution velocity of oxygen from air passed into sodium carbonate is calculated from the oxidation rates of sodium sulphite and stannous hydroxide in the same liquid. There is a negative induced reaction, the oxidation of stannous hydroxide having an inhibiting action on the oxidation of the sulphite. The rate is independent of the quantity of sulphite present and the influence of the concentration of sodium carbonate is very small.[28]

Heterogeneous Liquid-Gas Decomposition.

$$2NaHCO_3 \text{ aq.} \rightarrow Na_2CO_3 + CO_2 + H_2O.$$

The rate of change of composition of bicarbonate solution into which carbon dioxide was being passed indicated that the decomposition of bicarbonate in aqueous solution is a unimolecular reaction (first-order reaction) in which the diffusion velocity of the liberated carbon dioxide is the rate-determining factor, and the thickness of the diffusion layer is governed in the initial stages by the concentration of carbon dioxide. The reaction in solid bicarbonate has a more complicated mechanism (see below). The activation energy of the diffusion process is 9733 g.-cal.[29] In the absence of a solid phase and without the passage of carbon dioxide the hydrolysis of CO_3^{2-} must be considered. Concentration-time curves for HCO_3^- and CO_3^{2-} show that with increasing initial concentration the total duration of decomposition increases because of hydrolysis. The reaction calculated from the half-life period is monomolecular with $K = 0{\cdot}0286$. Passage of carbon dioxide-free air through the boiling solution accelerates the reaction, but at a decreasing rate with increasing initial concentration, the reaction order remaining monomolecular. Coarsely dispersed solids (calcium carbonate, graphite, nickel, etc., grain size < 0•06 mm.) do not accelerate the decomposition as they do with calcium bicarbonate. On the other hand, lyophobic colloids accelerate the decomposition of sodium bicarbonate but retard that of calcium.[30]

The first-order nature of the reaction is confirmed by an application of van't Hoff's differential method. The alkaline-earth bicarbonates, however, decompose in a second-order reaction.[31]

Heterogeneous Solid → Gas Reaction.

$$NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O.$$

By use of the thermobalance it was shown that the reaction proceeds from a first-order reaction in the initial stage, but is disturbed by the adsorbed water vapour, becoming of zero order and then changing to a two-thirds order.[29]

Homogeneous Reactions in Solution.

Iodine and Sodium Carbonate.

In the system $c(0{\cdot}010\ I_2 + 0{\cdot}24\ KI + 0{\cdot}20\ Na_2CO_3)$ at 18·5°C., the time in min. required to complete the formation of half the iodate, t, is with $c = 1$, 50 min., with $c = 0{\cdot}5$, 11 min., and $c = 0{\cdot}25$ it is 3 min., but with caustic soda the rate of disappearance of free iodine is very rapid and increases with the concentration of hydroxide. In an alkaline medium the iodine is transformed into iodate by different mechanisms depending on the degree of alkalinity.[32]

Calcium Sulphate and Sodium Carbonate.

The reaction $CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4$ in aqueous solution is second-order. For a total concentration of 2·53 mg.-ion/l., k_2 is 0·00208. At this concentration the speed of the reaction was increased one-hundredfold by the addition of 1 g./l. of calcium carbonate; but the activating effect decreases considerably with increase in initial $[Ca^{2+}]$.[33]

Heterogeneous Liquid–Solid Reactions.

The kinetics of the reaction $Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2KCl$ were investigated in degassed solutions containing 10% alcohol at 25, 30 and 35°C. The solutions were stirred continuously and at 30 sec. intervals samples of the precipitate were removed, washed in alcohol, dried and examined by Debye-Scherrer patterns. The product is vaterite, the most unstable modification of calcium carbonate; the nascent vaterite in contact with water reverts to calcite or calcite and argonite in a few minutes. The pure anhydrous product is however, stable and it is converted to calcite only by pyrolysis above 350°C. The measurements are concerned largely with the transformation of vaterite and need not concern us here, although it is of interest to remark that the apparent stability of a metastable form is shown to be not a fundamental characteristic but dependent on numerous factors such as the presence of nuclei, size and perfection of crystals, impurities, etc. (See 'Inorganic').

Some aspects of the reactions between a solid phase and a liquid or gaseous phase are discussed in an important paper. The importance of the ratio between the volumes of solid products in the initial and final states of reaction is stressed in the concept of equivalent volumes'. According as to whether this ratio is greater or less than unity, the solid phase formed protects or does not protect the initial phase. Defining $\Gamma = V_a/V_b$ the ratio of the equivalent volumes of the initial and final products, we find that in the reaction $BaCl_2(s) + Na_2CO_3 aq.$, $\Gamma = 0{\cdot}83$ but for $BaCl_2 aq. + Na_2CO_3(s)$ $\Gamma = 1{\cdot}07$. In the first case the penetration of the solution into the mass of barium chloride is total in a few hr., but in the second the penetration is of the order of 0·3 cm. at the end of 2 months with decreasing speed. The ratio of the velocities of penetration is of the order of 500. With $Na_2CO_3 aq. + CaSO_4,2H_2O (s) \rightarrow Na_2SO_4 aq. + CaCO_3(s) + 2H_2O$, Γ = equivalent volume of calcium carbonate/equivalent volume of gypsum = 0·5. It is therefore very favourable to a total penetration of gypsum by aqueous sodium carbonate.[34]

Aqueous Sodium Carbonate and Silica.

The solubilities of superficial layers of quartz and powdered silicates in carbonate solutions were determined, and solubility curves, $\Sigma q = f(\Sigma t)$ were constructed, q being the amount of silica dissolved in a definite time, t, when

500 mg. (85–50μ) of powder were agitated with 20 ml. of solution in a closed tube at 20°C. The solubility rate decreases rapidly during the first hours of extraction and tends to reach equilibrium. It has no relation to the amount of silica in the solution which is always far from saturation. After a one-day treatment with 0•1 M. sodium carbonate + 0•1 M. sodium bicarbonate, the following values were obtained for m/M (minimum mass removal/total mass): vitreous quartz 14, quartz 28, orthoclase 25, albite 27, labradorite 32 (all × 10^{-5}).[35]

The amount of silica removed by boiling 100 ml. of the given liquid in a silica flask has been determined colorimetrically. For caustic soda it was proportional to the concentration and was approximately in mg./cm.^{2} of surface 0•364 pH –0•4206; sodium carbonate gave a similar result but weaker.[36]

The action of carbon dioxide on aqueous sodium silicate at temperatures below the critical point shows that the soda–carbon dioxide combination is more stable at low temperatures than the soda–silica. On cooling silica is liberated from the latter combination by the action of carbon dioxide, so that single crystals of α-quartz may be produced at constant temperature.[37]

The attack on Jena glass by mixed solutions of caustic soda and sodium carbonate (0•1 to 2•0 N.) is a linear function of the time and is therefore not a diffusion phenomenon. The susceptibility to attack was lower for solutions of lower concentration indicating perhaps some concurrent adsorption.[38]

Solid–Gas Reactions.

The rates of decomposition of sodium and other carbonates in a stream of nitrogen were studied in the absence or presence of water vapour and solid promoters at various temperatures between 200° and 700°C. Water vapour and the solid promoters (SiO_2, Al_2O_3, $Al_2O_3,2SiO_2$) all increase the rate individually and still more in combination. $Al_2O_3,2SiO_2$ has the greatest effect in the absence of water; generally water vapour has a greater effect on the decomposition of sulphates and solid promoters on the decomposition of carbonates.[39]

(Heterogeneous) Solid–Solid Reactions.

The reaction of sodium carbonate with metakaolin to form carnegieite has been investigated in connection with the diffusion in solid phases over geological times. In 10^8 years the layer thickness of carnegieite produced in this manner should be 1000 cm. at 700°C., 60 cm. at 600°C., 1•8 cm. at 500°C. It seems that diffusion alone in solid phases cannot transport matter over long distances.[40] The velocity constant is related to temperature by the expression $k'' \simeq (8 \times 10^{14}) \times \exp(-95{,}000/\mathbf{R}T)$ g.^{2} cm.$^{-4}$ hr.$^{-1}$ and $\Delta m^2 = k''t$. Δm is the quantity of sodium oxide diffused during the time of the experiment.

Sodium Carbonate and Calcium Carbonate.

Calcite and soda heated to 700°C. in an atmosphere of carbon dioxide for 90, 270, 400 and 580 min. showed a distinct reaction zone at the boundary between the solids, and the width increased with duration of heating. The diffusion layer in the soda is wider and less sharply defined than in calcite. Additionally the soda pellets were marked on the surface with tiny gold-leaf fragments, pressed on to a calcium carbonate layer and heated in carbon dioxide in an electric furnace at 650°, 700° and 750°C. The reaction layer was studied microscopically, with X-rays and by chemical analysis, and the position of the gold markers determined. The results were the same as with the calcite crystals. The mutual diffusion of Ca^{2+} and Na^+ ions results in the formation of $Na_2Ca(CO_3)_2$. The kinetic constant $k = (\frac{1}{2})v(z^2/A_x^2)$. $(1/t)(\Delta m)^2$ was found to be 6•1 × 10^{-10}, 4•0 × 10^{-10} and 1•1 × 10^{-10} equiv. cm.$^{-1}$ sec.$^{-1}$ at 750°, 700° and 650°C., respectively; the calculated values are 4•2, 2•4 and 1•0 equiv. cm.$^{-1}$ sec.$^{-1}$ (v = equiv. volume of the reaction product (20•6), z =

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valence of the migrating ion (1 and 2), A_x = ionic weight (23 and 40), and m = amount of Ca^{2+} and Na^+ in g./m.^{2}.[59] (See section on Physical Properties).

Sodium Carbonate and Silica.

This most important reaction has been the subject of many researches. The reaction velocity qualitatively may be said to increase with decreasing size of grain, although differences tend to disappear as the temperature rises. The insulating effect outweighs the effect of increased surface. With larger particles the insulating effect is greater; it disappears on sintering when the finer the grain, the more rapid is the action.[41] The reaction velocity also increases as the sample amount becomes smaller. The maximum value of k in rate %/min. for $SiO_2 \rightarrow Na_2SiO_3$ is 0·083%/min. and for $SiO_2 \rightarrow Na_4SiO_4$ is 1·85%/min. both measured at 800°C.[42,43] The rate, k, of the reaction between β-quartz and sodium carbonate has been determined, and from a plot of the maximum k values for certain temperatures the experimental initial temperature of the reaction was measured; for sodium carbonate (calculated) it is 1910°C. The calculated and experimental initial temperatures for the formation of Na_2SiO_3 (I) are 300°, 320°C., for Na_4SiO_4 (II) 598°C., –; for $Na_2Si_2O_5$ (III) 187°, 320°C. The secondary reactions of sodium carbonate with I to form II and with III to revert to 2I start at 870° and 470°C., respectively, and the corresponding values of ΔH are 43·87 and 25·1 kg.-cal./mole and of ΔS are 38·2 and 33·5 g.-cal./mole/deg. (See section on Inorganic Chemistry).

The reaction between $1Na_2CO_3$ and $3SiO_2$ appears to be of the first order. The effect of a change in the crystal structure of quartz upon the course of the reaction has been discussed.[44] It has been shown that the effective temperatures of a number of reactions between solids occur roughly at 0·9 times the melting point on the absolute scale; the more complex the compounds the nearer the melting point before activity begins. The lowering of the reaction temperature by the addition of other substances to form a flux follows the melting-point lowering, which may be great for high temperature reactions; quartz + barium carbonate + sodium carbonate begins to react at 400–450°C.[45]

The reaction rate is shown clearly by examining the statistical distribution of reacted silica particles, compared with the nonreacted before the experiment, in mixtures heated for 6 hr. at 400°, 600° and 800°C.[46]

The rate of the reaction $Na_2CO_3 + Na_2O{,}2SiO_2$ is smaller than with $Na_2CO_3 + SiO_2$, but is considerably accelerated above 840°C. when a eutectic melt phase is formed, and above 865°C. is equal to that of quartz and sodium carbonate at 900°C. It appears that reactions between solid crystalline compounds and melts are determined much more by the physical conditions in the system than by chemical factors alone. The activation energies for the reaction $Na_2O{,}2SiO_2 + Na_2CO_3$ are for the solid–solid reaction 149,000 g.-cal. and 94,000–97,000 g.-cal. if the melt phase is present. These energies are not so much related to the heat effect but to diffusion, surface tension, wetting, viscosity factors, etc.[47]

The influences of mixing ratio and temperature change on the reaction rate in the Na_2CO_3–SiO_2 system have also been examined by the thermal balance. The reaction velocity can be expressed in the first place by $-\log(1-Fx) = Kt$, where x is the reacted fraction, t the elapsed time, K the rate constant (a function of the alkali diffusion coefficient and the quartz grain size), and F is the ratio $[Na_2O]$ in mixture/$[Na_2O]$ on silica grain surface; F is < 1 in the region investigated.[48-50] In a continuing paper the decomposition of carbonate and diffusion of alkali were assumed to be rate-determining and the following equation was derived:

$$\tfrac{1}{3}(1-Fx_S) - \tfrac{1}{2}(1-Fx_S)^{2/3} + \tfrac{1}{6} = kD(C_o-C_R)t/R_o^{\,2},$$

where R_o is the radius of a spherical particle of silica, t = time, C_o = concentration of Na_2O on the surface of the particle, C_S is initial concentration of Na_2O in the sample, C_R is concentration of Na_2O at the point of radius R of silica particle, x_S = apparent rate of reaction, F is C_S/C_o, D is the diffusion constant and k is a constant.[51]

The reaction $Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$ has been investigated by observation of the weight loss of the reacting mixture and by the measurement of the amount of unreacted silica. With particles of average diameter 0•072 mm. at 800°C. the process appeared to be controlled by the diffusion of sodium carbonate through the silicate. Metasilicate was obtained when the ratio SiO_2/Na_2CO_3 was less than 2. Above this value the orthosioicate, Na_4SiO_4, is formed. The addition of sodium chloride (3% of soda by weight) to an equimolecular mix at 750°C. changes the mechanism. A eutectic is formed ($NaCl$–Na_2CO_3) which helps in silicate formation, the reaction proceeding at constant concentration of reacting substances according to the equation $dG/dt = K_1(1-G)^{2/3}$. A second step begins when all the carbonate has gone into the eutectic, and the first-order rate is determined by the changes in sodium carbonate: $dG/dt = K_2(1-G)^{5/2}$. In the third step the quantity of liquid phase decreases but its concentration in sodium carbonate remains constant. The rate equation of the first step is approximately followed. Other experimental condtiions ($G \ll t$) can be chosen to obtain an initial constant rate $dG/dt = K_3$. G is the degree of transformation of substance, t is the time, $K_{1,2,3}$ are constants.[52]

Sodium Carbonate and Other Acidic Oxides.

Heated in a platinum boat in a tube furnace at 10°/min., sodium carbonate begins to decompose in the presence of aluminium oxide at 670°C., ferric oxide at 670°, silica at 560° and vanadium pentoxide at 450°C.[53]

Alumina and sodium carbonate have been allowed to react at various temperatures in a stream of oxygen. The only reaction product was Na_2O,Al_2O_3 and Jander's equation $(1-\sqrt[3]{1-x})^2 = kt$ holds, where x is the mole fraction of alumina that has reacted, k (a coefficient of reaction velocity) is $Ae^{-q/RT}$, A being a constant and q the activation energy (58,800 or 50,800 g.-cal., respectively, as T is below or above 1123°K., the melting point of sodium carbonate). k is independent of the ratio Na_2CO_3/Al_2O_3 but depends greatly on the streaming gas. The reaction proceeds very rapidly in steam with q = 58,800 g.-cal., and A about 100 times as great as for oxygen below 850°C., but is too fast to provide accurate data above this temperature. Steam applied in the practice of calcining aluminous clay in the soda-lime process reduces the calcining temperature by 100–150°C.[54]

The reaction velocities of sodium carbonate with (a) ferrous sulphide and (b) manganous sulphide are of interest in the desulphurization process for iron and steel. The reactions examined were $FeS + Na_2CO_3 \rightarrow FeO + Na_2S + CO_2$ and $FeS + Na_2CO_3 + H_2 = Fe + Na_2S + CO_2 + H_2O$ or with MnS replacing FeS. Both reactions proceed quickly with the second being much accelerated. The equilibrium value of the desulphurization ratio is higher at higher temperatures and best for a 1:1 mixture at fixed temperatures.[55]

Rates have been determined for the reactions between carbonate and mullite, silica and alumina from the evolution of carbon dioxide as a function of time. The rate generally is a function of grain size but the temperature coefficient is characteristic of the system involved. The reaction product lessens the period of reaction in accordance with the relation $dy/dt = k/y$ where y is the thickness of the reaction product layer. The carbonate here attacks mullite most easily, with less attack on quartz and least on corundum. The relation between the velocity of reaction and the temperature is $K = Ce^{-q/RT}$, where the constant C depends in part on the number of mobile particles and the physical state of the material, and q is the activation energy in calories for the movement of 1 mole of particles from point to point in the crystal lattice. For silica and sodium carbonate, $q = 120{,}800$ g.-cal./mole CO_2 and hence $K = 4{\cdot}081 \times 10^{20}e^{-60770/T} \simeq 0{\cdot}575 \times 10^{-5}$. For mullite (1:1) $q = 75{,}550$ g.-cal. and $K = 1{\cdot}523 \times 10^{12}e^{-38{,}000}/T$.[56]

The rates of solution of pitchblende (as U_3O_8) in soda solutions have been measured over a wide range of conditions. The specimens, of measured surface area, analyzed U_3O_8 62·4, SiO_2 19·4, Pb 11·4, S 0·62, CaO 3·4%. The rate-controlling step is a heterogeneous surface process rather than a homogeneous reaction in solution. The oxygen participating in this is disassociated rather than molecular, since the rate depends on the square root of the oxygen pressure. While the presence of some CO_3^{2-} and HCO_3^- is necessary for the solution of U_3O_8 to take place, these ions do not appear to act directly in the rate controlling step of the reaction, since large increases in their concentration have no effect on this. Their role seems to lie rather in preventing back and side reactions such as hydrolysis and reprecipitation. (See Utilization).

Exchange Reactions.

In a solution approximately 0·03 M. in carbonate tetrammine cobaltic nitrate $[Co(NH_3)_4CO_3]NO_3$ and 0·01 M. in sodium carbonate containing a small amount of ^{14}C, exchange occurs at 20°C. in the dark with a half life of 7 hr. The reaction shows first-order characteristics.[57]

With carbonatopentammine cobaltic nitrate, $[Co(NH_3)_5CO_3]NO_3$, the rate of exchange of free and complexed CO_3^{2-} in aqueous mixtures of ^{14}C-labelled sodium carbonate and bicarbonate has been measured as a function of reactant concentrations, pH and temperature. Two concurrent processes were postulated, one ionic, of direct collision, the other of aquation, *i.e.* the displacement of the carbonate ion by water molecules. The primary step in the latter is the addition of hydrogen ion to form the corresponding bicarbonato-complex. Detailed mechanisms of aquation based on rupture of either the Co–O or C–O bond within the carbonato complex were equally consistent with the kinetics observed in the pH range 8–10: studies of the influence of ionic strength on the exchange rate tend to favour the former.[58]

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ANALYTICAL CHEMISTRY OF SODIUM CARBONATE AND BICARBONATE

Sodium Carbonate as an Analytical Standard

Recommended specifications for sodium carbonate and bicarbonate as guaranteed reagents are given in an American investigation. The following should be the percentage upper limits of impurity in the bicarbonate: insoluble matter 0·020, chloride 0·003, sulphate 0·003, phosphate 0·002, potassium 0·02, ammonia 0·0005, calcium, magnesium or ammonium hydroxide precipitate

0·010, heavy metals Pb 0·0005, Fe 0·001. Percentage limits for the carbonate are: insoluble 0·020, chloride 0·005, sulphate 0·004, nitrogen 0·001, phosphate, 0·002, ammonium hydroxide precipitate 0·010, silica 0·005, calcium and magnesium 0·015, potassium 0·02, arsenic 0·0003; loss on ignition 1%.[1,2]

The conversion of the bicarbonate into the carbonate for an analytical standard seems to be re-examined from time to time. It is converted quantitatively into the carbonate at 250°C. if heated in a platinum crucible and stirred with a platinum wire.[3,4] Sodium carbonate is stable at all temperatures between 20°C. and 200°C.[6] Pure electrolytic silver is the best ultimate standard, but pure sodium carbonate, iodine, arsenious oxide and dichromate are convenient and adequate working standards.[7]

Iron-free sodium carbonate is prepared by dissolving 40 g. of the anhydrous salt in 100 ml. of hot water, filtering, shaking the filtrate with 50 ml. of industrial alcohol at 50°C. in a stoppered flask, cooling to room temperature, decanting, and repeating the extraction with 50 ml. more alcohol. The resulting monohydrate is dehydrated without fusion by heating to not over 250°C. Iron may be removed from the original water filtrate by adding dilute permanganate and ammonia, heating in the steam bath with a few drops of alcohol to reduce the permanganate, and filtering.[8]

For pharmaceutical requirements sodium carbonate may be qualitatively analyzed for free alkali or bicarbonate by taking a 1:5 or 50:50 solution, adding 30 ml. of barium nitrate solution and 3 drops of phenolphthalein, and allowing to stand well stoppered for 3 min.; the solution should be colourless, but coloured a permanent red by 0·1 ml. of 0·1 N. sodium hydroxide.[9] This requirement is sensitive to 0·025% of free base or 0·1% of bicarbonate. The methods of several pharmacopoeias for the determination of carbonate in bicarbonate have been reviewed and slight technical modifications suggested in a Portugese paper.[10] Sulphate impurity in reagent-grade sodium carbonate may be determined nephelometrically by the addition of solid barium chloride reagent to solutions of the sample containing 20% of ethyl alcohol. A standard addition and extrapolation procedure is employed, permitting the estimation of the sulphate content and providing a permanent calibration curve specific to the salt (calcium carbonate, sodium carbonate or potassium chloride) used. At a concentration of 0·1 g./ml. differences of 0·0002% SO_4 are detectable unambiguously. The method may be applied to a SO_4 range of 0·0002 to 0·010%. Prior filtration of the solution is required when the SO_4 concentration is below 2·0 γ/ml.[11] When sodium carbonate is present the following procedure may be adopted for the determination of sodium hydroxide: dilute the solution to 100 ml. with carbon-dioxide-free water; in an aliquot part determine the total alkalinity by titration with hydrochloric acid and methyl orange; add another portion from a pipette to 25 ml. of a solution containing sufficient barium chloride to precipitate all the carbonate ion present and leave the solution about 0·1 N. in excess barium; shake, add a little phenolphthalein and titrate the hydroxide with hydrochloric acid in presence of the barium carbonate precipitate.[12] A simpler method is to decompose the sample by boiling with dilute sulphuric acid, collecting the carbon dioxide in 0·1 N. sodium hydroxide containing 1% of barium chloride and titrating the excess hydroxide with 0·1 N. hydrochloric acid. The difference between this and a blank titration gives the sodium carbonate.[13]

The preparation of sodium hydroxide solutions free from carbonate may best be done by treatment with barium hydroxide or a barium salt, or by Sörensen's method of making a 1:1 solution of caustic soda, boiling and allowing to cool slowly, when practically all the carbonate is precipitated and the supernatant liquid may be syphoned off. Carbonate present, if not less than 0·03%, may be determined with high precision by titrating 45 ml. of the alkali to about

0·05 ml. less than required for complete neutralization and finishing with 0·01 N. hydrochloric acid until the faint pink colour is just discharged. A known amount of 0·01 N. hydrochloric acid is then added and the solution boiled under a reflux in a current of carbon-dioxide-free air. A soda-lime tube is fitted, and the solution is cooled with running water, and back titrated with 0·01 N. sodium hydroxide.[14]

Technical Analysis

The determination of sodium carbonate in a charge containing pyrolusite and pyrites cinders for aluminomagnesic and lime-soda glasses can be done by shaking a sample with hot water and titrating to a phenolphthalein end point with standard 0·5 N. nitric acid.[15] 'Boiler compound' is a mixture of sodium carbonate, disodium hydrogen phosphate and starch. The problem is to determine the phosphate simply and quickly; an aliquot sample is titrated with standard sulphuric acid until methyl purple indicator turns green; a slight known excess of acid is added, the total volume being recorded; carbon dioxide is boiled off and the sample titrated with standard sodium hydroxide of the same normality to the first appearance of the green colour; phenolphthalein is added and the titration continued to a pink colour. We have: (total volume in ml. H_2SO_4 - equivalent volume in ml. of NaOH)×(normality) × 0·053 = g. Na_2CO_3. The phosphate can be determined in the same sample by back titration with standard sulphuric acid through the green to a definite purple. The volume of sulphuric acid required corresponds to the phosphate content. The presence of either sodium hydroxide or trisodium phosphate will interfere, but their presence can be detected by the initial pH of the solution.[16]

The total chlorine in the chlorination products of sodium carbonate may be determined by reducing the sample with sodium nitrite in the presence of nitric acid and titrating with silver nitrate.[17]

Sodium bicarbonate in self-raising flours containing chalk (B.P.) is usually determined by treating a sample with 6 N. sulphuric acid and measuring the volume of carbon dioxide evolved coming from both calcium carbonate and sodium bicarbonate. If a 2·5% solution of disodium dihydrogen pyrophosphate which has pH = 4·0–4·2 is substituted for the dilute sulphuric acid the bicarbonate in a flour is completely decomposed but the chalk is not.[18] The excess sodium bicarbonate in baking powder may be determined by the following method: when the aqueous solution is neutralized to methyl orange by normal acid, 1 ml. of acid is required for each millimole of bicarbonate and again for each millimole of disodium hydrogen phosphate in the solution; if it is then treated with aqueous calcium chloride to render the end-point sharp in the presence of tartrates and titrated with caustic soda and phenolphthalein, a measure is obtained of the total amount of soluble phosphates converted into the primary form by the first titration. If m ml. of normal acid are used in the first titration and p ml. of normal alkali in the second, then $m - 0{\cdot}5p$ is equal to the number of millimoles of bicarbonate present, or 0·08401 $(m - 0{\cdot}5p)$ = grams of $NaHCO_3$.[19]

A good mixed indicator is available for soda-ash titrations: 6 vols. of 0·1% thymol blue, 1 vol. of 0·1% cresol red, and 14 vols of 0·1% bromocresol green are mixed; 6 drops of the mixture may be used for 100 ml. of sodium carbonate solution. A clearly distinguishable colour change occurs at pH $\simeq$ 4.[20] The caustic soda and sodium carbonate content of feed waters can be determined by the phenolphthalein (p) and methyl orange (m) method: NaOH = $(2p-m) \times 0{\cdot}4$ mg./l. and $Na_2CO_3 = (m-p) \times 0{\cdot}106$ mg./l.[21] The phenolphthalein end-point in these and similar titrations is at pH = 8·3 and the methyl orange at pH = 4·1. A little alkali silicate does not interfere but if any of the phosphates or arsenates Na_3PO_4, NaH_2PO_4, Na_3AsO_4 and Na_2HAsO_4 are present they must be determined separately (or the phosphates partly, as above)[19] since sodium carbonate and trisodium arsenate and phosphate all react with 1 mole of hydrochloric acid to give the phenolphthalein end-point, and with 2 moles to give the methyl orange end-point. If much sodium silicate is present it probably reacts with bicarbonate to give silica, sodium hydroxide and sodium carbonate. Instead of using the above indicators the Beckman titrimeter can be set at the proper pH before each titration.[22]

The course of the reaction can be closely followed in the high-frequency titrimeter, the beaker containing about 100 ml. of solution being placed in the oscillating coil. Such an arrangement is remarkably sensitive to hydrogen- and hydroxyl-ion concentration.[23]

Bimetallic electrodes (Sb–HgCu, Sb–Pb, Cu–CuO etc.) appear to have some advantages in electrometric titrations, the antimony–amalgamated copper being best for general use. Curves are given for various acid-base relations, sodium carbonate and hydrochloric acid giving two end-points. The composition of precipitated hydroxides and basic salts may be determined but some 60 secs. are required to reach constant e.m.f.[24] The use of a polarized platinum electrode in the electrometric analysis of sodium carbonate has been studied; it gives two pronounced inflection points.[25] The antimony electrode may be used in the titration of the dark liquors of the pulping industry. Before the determination of sodium carbonate, sodium hydroxide and sodium acetate or similar salt, hydrogen peroxide is added to the solution to destroy sulphide ion. The antimony electrode then establishes the equivalent points on titration: (1) pH = 7·6 (for NaOH + $\frac{1}{2}Na_2CO_3$ after addition of saturated aqueous barium chloride for NaOH alone) and (2) pH = 3·5 (for NaOH + Na_2CO_3 + NaR in 50% aqueous ethyl alcohol; R is AcO^- or similar anion). Antimony may also be used as a reference electrode dipping into a buffer solution of pH 7·6 or 3·5.[26]

The amperometric determination of sulphate ion in sodium carbonate or bicarbonate mixtures can rapidly be performed with a lead salt after addition of nitric acid to destroy the carbonate and to make the solution just acid to methyl red.[27]

Iron in small amounts in sodium bicarbonate may be determined electrolytically. 25–30 g. of the sample are dissolved in 100 ml. of water, and 3–8 g. of tungsten trioxide, 7–8 g. of Rochelle salt, 4 g. of glucose and 40 mg. of Cu as aqueous copper sulphate are added. The contained amount of iron in given samples of bicarbonate was between 0·0005 and 0·0026%.[28] The iron is deposited on the platinum electrode as the copper-tungsten-iron alloy, which is then dissolved and the iron determined iodometrically.[29]

The Karl Fischer method may be used for the determination of water in sodium bicarbonate. The moisture is extracted from the sample with dry methyl alcohol, which is filtered and an aliquot portion of the extract is titrated with the Karl Fischer reagent (a methyl alcohol solution of iodine, sulphur dioxide and pyridine in which we have approximately $H_2O + I_2 + SO_2 + CH_3OH \rightarrow 2HI + CH_3HSO_4$); the dissolved bicarbonate is afterwards determined acidimetrically for use as a correction in the Karl Fischer titration. 100 g. of the bicarbonate sample are vigorously shaken with 130 ml. of methyl alcohol; after settling 100 ml. of the extract are taken and a 50 ml. aliquot is titrated directly with the standardized reagent, which measures moisture plus dissolved bicarbonate; the latter is determined in the other 50 ml. aliquot by titration with 0·1 N. hydrochloric acid.[30]

The ratio of iodine pentoxide to sodium carbonate has been utilized in atomic weight determination; the end-point for the reaction of iodine pentoxide with the carbonate was found with bromothymol blue after carbon dioxide had been expelled. The ratio $I_2O_5:Na_2CO_3$ is 3·14950, giving the atomic weight of iodine as below 126·92 and that of carbon above 12·00.[31]

Magnesium in alkali products generally may be determined photometrically with Thiazole Yellow. Aluminium, copper, iron, manganese and nickel are removed by chloroform extraction of their oxinates; removal of calcium and decrease in sodium chloride concentration are obtained by treatment with sulphuric acid in 98% methyl alcohol solution. A stabilized magnesium dye lake is obtained with Thiazole Yellow. The results are accurate to within 2 to 5%.[32]

Co^{++} ions react with peroxy-acids in the presence of alkali bicarbonate to form a complex which exhibits maximum absorption at 260 and 440mμ. The band at 260mμ shows greater sensitivity. Beer's law is followed for 0 to 8p.p.m. of cobalt. The colour is developed by treating a neutral cobaltous solution with hydrogen peroxide and saturated bicarbonate solution. There are some interfering ions.[33]

A number of stable colorimetric scales for the rapid exploration of the feeble acid-alkaline zone have been devised for use in the assay of hydrolyzable salts of importance in pharmaceutical chemistry. The stable bromothymol-blue scale (pH = 6·0–7·6) is considerably extended by the use of mixtures of cobalt chloride with acetic acid or potassium dichromate, giving pH = 4·4 to 8·4. By means of these scales the requirements for the neutrality of aqueous solutions of sodium bicarbonate, sodium acetate, and alkaloidal salts for injection may be accurately checked.[34]

Alkali carbonate and sulphide mixtures are of technical importance in the paper and allied industries. 20–40g. of a sample may be dissolved in 1 l. of water. A suitable aliquot is taken and diluted to 150ml., and carbonate, sulphate and sulphite are precipitated with barium chloride solution, filtered and washed. The precipitate is then dissolved in a measured volume of 0·5 N. hydrochloric acid and 0·1 N. iodine solution; the sulphite is thus oxidized to sulphate, and equivalent acid is released. Excess iodine and acid are titrated: the sum of acid and iodine used is equal to the carbonate in the sample (usually about 1% Na_2CO_3)[35] Other details for the determination of caustic soda, sodium carbonate and sodium sulphide in such spent liquors, together with examples of calculations and actual determinations, are available.[36]

Methods are available for the determination of carbonate and bicarbonate in some complex mixtures of technical importance e.g. chlorine bleaching solutions,[37] cyanide–zinc plating solutions.[38]

In the fusion of silicates with sodium carbonate in a platinum crucible there is often some loss of iron. This is apparently caused by the reduction of iron compounds to metallic iron which alloys with the platinum. Such losses can be prevented by heating at 1200°C. in a well ventilated electric muffle, but gas burners designed so that no reducing gases enter the crucible are also effective.[39]

Qualitative Applications

The removal of phosphates in qualitative analysis by boiling with 5–15% aqueous sodium carbonate for half an hour, with subsequent filtration and washing, is not recommended for precise work. The phosphates of manganese and calcium are scarcely attacked, and those of chromium, strontium and magnesium are only half removed; it is effective only with iron and barium. Furthermore, the sodium phosphate formed may react on metal carbonates or oxides in the presence of sodium carbonate to give metallic phosphates.[40] The reaction between calcium triphosphate and sodium carbonate, and also with the bicarbonate, has been studied at 100°C. Monocalcium hydrogen phosphate and sodium carbonate (as do also disodium hydrogen phosphate and calcium carbonate) react in the presence of an excess of base to produce an insoluble quaternary phosphate, particularly if carbon dioxide is removed by passing a current of steam through the mixture. The initial content of trisodium phosphate in the solid phase increases with increasing concentration of reactants; some of this trisodium phosphate may be removed by washing. It seems therefore that the preparation of a sodium-free $CaHPO_4$ or $Ca_3(PO_4)_2$ is hardly possible in the presence of sodium salts. The phosphoric acid content of the solid phase and that of the solution exert only an indirect influence on the carbon dioxide content of both phases; the phosphoric acid content of the solid phase varies between fairly narrow limits. Even after several treatments with cold saturated aqueous sodium carbonate it does not fall below 30%; the calcium carbonate content does not exceed 22%. A complete separation of phosphoric acid and calcium carbonate by boiling with sodium carbonate is therefore impossible. The carbonic acid content of the solid phase appears to be proportional to the ionized carbonic acid in solution.[41]

The accuracy in determining carbon dioxide by absorption in soda lime is increased by using soda-asbestos in addition.[42] A trace of water is needed. Absolutely dry reagents absorb less carbon dioxide, and potassium hydroxide is inferior to sodium hydroxide. Granules of 14–26 mesh are preferable.[43]

The titration of acid and alkali can be performed in a high-frequency electromagnetic field, the energy input to the sample being measured. The electromagnetic field produces ionic motion and dipole rotation in a solution resulting in the absorption of energy which provides an indication of the end-point and obviates the introduction of electrodes. The process is described in a patent specification which gives the circuit diagram and titration curves for, amongst others, sodium carbonate and hydrochloric acid. A combination pH meter for electrometric titrations is also patented.[44]

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UTILIZATION OF SODIUM CARBONATE

World Production of Soda Ash

Table XXIX gives an estimated total annual output of soda ash in thousands of metric tons over the first half of the century.[1]

TABLE XXIX.- WORLD PRODUCTION OF SODA ASH

Year	Production (thousands of metric tons)
1865	375
1875	525
1885	800
1895	1250
1905	1900
1915	2700
1925	4100
1935	6000
1940	7000

The distributed production (again in thousands of metric tons) among the more important countries, in recent years, appears in Table XXX.[2]

TABLE XXX.- DISTRIBUTION OF SODA ASH PRODUCTION AMONG COUNTRIES

Year	USA*	USSR	W. Germany	France	Italy	Japan±	Spain	China
1946	3887	257	-	481	180	22	63	-
1951	4621	824	836	819	520	226	100	0·2
1955	4452	1437	983	781	472	377	128	1·7

* Includes natural soda, perhaps 4%

± If crude soda is included these figures are almost doubled.

It is not certain how the above figures have been obtained nor what reliance may be placed upon them. No details seem to be available for the British or Canadian industry.

A general survey of the world's ammonia-soda plants up to 1941 is available, together with an estimate of their daily capacity.[1]

It would be interesting if it were possible to establish some correlation between the fluctuations in output shown in Table XXX and economic conditions within a country or more generally throughout the world. Recent estimates for the United States[3] appear to be slightly in excess of those in Table XXX but are interesting in that natural soda production for 1957 at 676,611 metric tons is greater than in 1956 when it was 654,890; whereas synthetic soda fell from 4,997,579 to 4,650,588 metric tons in the same period.

The estimated distribution of soda ash among industries in U.S.A. in 1940 and the actual in 1953 is given below; the figures are in thousands of metric tons.[1,4]

	1940	1953
Glass	904	1590
Caustic and bicarbonate	780	790
Other chemicals*	710	1350
Soap	182	101
Cleansers	135	160
Pulp and paper	111	330
Exports	61	160
Textiles	45	40
Water Softeners	32	120
Petroleum refining	12	
Non-ferrous metals		430
Miscellaneous	185	226
Total	3157	5330

Other chemicals* (consuming soda ash)	
$CaCO_3$	190
Sodium chromates	110
Sodium hydrosulphite	13
Sodium nitrate	170
Sodium phosphate tripolymer	350
Dibasic sodium phosphate	70
Tetrabasic sodium phosphate	65
Other phosphates (tri-, mono-, meta- and pyro-)	34
Sodium silicate	230
Sodium sulphite	45
Sodium thiosulphate	15
Remainder	58
Total	1350

The main industrial outlets for sodium carbonate are discussed below under appropriate sub-headings. To a large extent this section must necessarily be a survey of the Patent literature for the period.

Catalysis.

Sodium carbonate finds much use as a promoter, for example, for inexpensive iron catalysts in the synthesis of hydrocarbons from carbon monoxide and hydrogen, particularly in fluidized beds,[5] and in vapour phase purification of organic substances by oxidation of impurities to carbon monoxide and water.[6] Sodium carbonate is also used in procedures where several catalyst beds are formed one above another and working at increasing temperatures: in one example the third of four different beds contains Co 31 on '*Filtercel*' 63, MgO 1·8, ThO_2 1·5 and Na_2CO_3 1·7%, functioning at 420°F.[7] More complicated treatment may be given to the iron catalyst by reducing the oxide to a determined oxygen content first by hydrogen at 480–810°C., then at 260–370°C. until the catalyst contains 3–10% by weight of oxygen; it is then 'precarbided' with a mixture of hydrogen and carbon monoxide at 260–370°C. until a proportion is converted into iron carbide. The iron oxide is impregnated before treatment with sodium carbonate or other promoter.[9]

Activated carbons promoted with sodium carbonate or other sodium salts of the same type are effective catalysts for naphtha reforming, since the promoter retards cracking and aids dehydrogenation, giving a product high in olefins and aromatics. The effect is largely specific since potassium hydroxide or carbonate has an adverse effect, while lithium carbonate catalyzes the water-gas reaction but does not promote reforming activity.[8]

The activation of fuels by sodium carbonate has been the object of much research. At 1000°C. it seems that the reactivity and the migration of alkali from the fuel bed are limited by reaction of the alkali with alumina and silica in the ash. For a coke containing 6•2% of ash as much as 3% of carbonate is required for maximum activation. The addition of lime eliminates the effect of the ash by displacing alkali from combination with alumina and silica. Maximum activation may then be obtained by adding 2% of CaO and 0•5% of Na_2CO_3; 50% of the alkali then migrates from the fuel bed.[10] The use of the process before carbonization had been hindered by fear of attack by the alkali on the retort and coke-oven refractories. Coke from full scale ovens quenched with sodium carbonate solution (12 tons of the decahydrate dissolved in about 23,000 gallons of water) gave a product containing about 3•8% of carbonate distributed uniformly through the coke, but with no general whitening; the physical properties of the coke are not appreciably affected. It has been suggested that in addition to the production of producer and water gas it would be preferable for household use.[11] The glow in a burning fuel bed is due to the oxidation of carbon monoxide and depends largely on the rate of air flow and the quantity of water vapour present in the air; the intensity can be increased by pretreatment with sodium carbonate or cupric chloride.[12]

The net effect of the addition of sodium carbonate to carbon is to increase the vapour pressure of the latter some 10^{15} times (see section on Inorganic Chemistry). In the producer-gas reaction the impregnated coke gives much richer carbon monoxide content; with water gas a product richer in carbon monoxide and hydrogen is obtained, but the increased reactivity of the fuel bed could be disadvantageous during blowing and offset any gains made during steaming.[13]

In coking high-sulphur coals laboratory experiments show that the addition of soda assists sulphur removal to a marked degree since coal containing 10% of combustible sulphur usually yields a coke with about 5–6%, but quite small quantities of soda reduce this to about 1•2%, and at the same time increase the reactivity and reduce the swelling tendency.[14,15] Bicarbonate may remove 56–57%.[16]

The rate of formation of carbon disulphide from sulphur vapour and charcoal has been studied in laboratory experiments with columns of sugar charcoal, birch charcoal and anthracite. The rate v is a linear function of time at 900° and 1000°C.; the addition of sodium carbonate (1% solution with subsequent drying) increases v from 0•334 and 0•777 g./min. at 900° and 1000°C. (sugar charcoal) to 0•776 and 0•82 g./min., respectively.[17]

Sodium carbonate is a fairly active catalyst in the oxidation of carbon by nitric oxide, as judged by the ignition temperature and the temperatures of appearance of carbon monoxide and carbon dioxide, a matter of some interest in the burning of propellants.[18]

In the carbonization of coal the addition of 2% of Na_2CO_3 gives a 24% increase in gas volume but the gas is of lower calorific value per cu. ft. The coke is said to contain more ash and more sulphur.[19]

In the hydrogenation of coal by heating with hydrogen under pressure, a milled mixture of ferrite and partially hydrated soda may be used.[20] The time of reaction in mild hydrogenation can be decreased by using aqueous sodium bicarbonate to the extent of 3•25 to 6•5% of the coal weight as a catalyst. The swelling of the coal is however reduced in this process.[21]

Gaseous mixtures of carbon monoxide and hydrogen are sometimes obtained by a two-stage process. Water gas is first produced by steaming finely divided carbonaceous matter in a fluidized bed (816–1093°C.), and then the char of high surface area from the first stage is impregnated with a catalyst (sodium carbonate or other alkali or alkaline earth carbonate) which promotes gasification with steam (704–982°C.)[22] The steam and carbon may be obtained from the pyrolysis of low grade oils.[23] The catalytic effect of soda in the reduction of carbon dioxide by charcoal makes a temperature reduction possible in the reaction zone of 150–200°C. by blowing in steam or flue gas. The quality of the gas is improved, the fuel consumption reduced and the effect of high temperatures on the generator is lessened.[24]

In laboratory-scale experiments heavy oil cracked on a refractory surface of magnesia blocks in the presence of steam shows a greatly accelerated steam–carbon reaction at an optimum temperature of about 870°C. when the blocks are impregnated with 5% by weight of sodium carbonate.[25] The rate of hydrogenation of coal is increased by sodium carbonate as a catalyst at 800–900°C.[26] In the hydrogenation of carbon monoxide at a pressure of 20–50 kg./sq. cm., a temperature of 150–225°C., and a velocity of 200–400 volumes of gas/volume of catalyst/hour, a precipitated iron catalyst promoted with sodium carbonate gave a reaction product containing 7–10% esters and 38–42% alcohols with 53–59% conversion of the carbon monoxide–hydrogen mixture.[27] Acetylene is obtained by the reduction of sodium carbonate with carbon at about 1100°C. to form carbon monoxide and sodium, which then react on the surface of steel balls at a temperature of some 700°C. to give sodium carbide and carbonate. Treatment with steam gives acetylene, and the carbonate is recovered with carbon dioxide.[28]

Kieselguhr may be lixiviated with water to remove soluble silicates; if the residue is dried, activated by fusion with sodium carbonate and washed with acid and alkali, it has decolorizing properties.[29]

Sodium bicarbonate (400 g., with calcium chloride 1550 g.) is applied to the initial degradation of potato starch (800 kg.) before autoclave treatment of the resulting powder.[30] In quantities of less than 2% it catalyzes the condensation of ϵ-caprolactam on heating in an autoclave with water vapour to give polyamide.[31] Mathematical relations have been established characterizing the starting, growing and degradation reactions in this process.[32]

Anhydrous sodium carbonate may be used as a catalyst in the trans-esterification of triethanolamine with coconut and soyabean oils.[33] The acrolein-paraformaldehyde condensation (1:4 moles) is accomplished at 50–65°C. with the aid of sodium carbonate to give a product imparting crease-resistance to textiles.[34,35] In quantities of 0·05 to 0·15% it has an accelerating effect on the emulsion and suspension polymerizations of vinyl chloride.[36] The relation between catalyst species and the constitution of formed resins has been investigated for phenol-formaldehyde-catalyst mixtures (1:1:0·02 moles) at 90°C. for up to 2 hr.; sodium carbonate was one of many catalysts examined.[37]

Production of Caustic Soda: The Causticization Process.

The fundamental reactions in the customary process are unchanged, but research and experience have shown that the extent of reaction and the amenability of the products to separation can be controlled by observation of simple mechanical precautions. Continuous operation at all stages of the process cycle utilizing mechanical equipment when possible assists control of the essential reaction and simplifies the duties of the operators and control chemists.[38] In particular a long tubular ball mill has been devised for this operation in which solid and liquid portions of the reaction product may be separated.[39] Heat exchangers play their part in the economy of the process; the use of reaction towers through which hot gases (air and steam) are blown has been patented.[40] A Russian investigation asserts that calcium carbonate precipitated and ignited to lime falls off in quality and after 5-10 ignitions has to be discarded.[41]

It is found that the presence of sodium sulphide and sodium sulphite decreases the degree of causticization, the amount depending on the concentration of the salts. The sulphite is causticized by lime but not the sulphide. Sodium thiosulphate does not affect the process and does not react with lime.[297]

For the Löwig process with ferrite, which has been extensively explored in Russia and Japan, see the section on Inorganic Chemistry.

Production of Cellulose and Fibres.

Lignin is removed during the bleaching of jute yarns resulting in reduced strength; if the yarn is pretreated with sodium carbonate and then after bleaching is impregnated with resins such as melamine-formaldehyde types an improvement in strength is noted.[42] The alkaline degradation of cellulosic fibres by sodium carbonate, etc. is reduced by the absence of oxygen and by the restriction of the high-temperature dyeing process to below 110°C.[43] Wool is modified by treatment with acetone and aqueous bicarbonate at 65°C. through a decrease of the cystine content to about half the original value and the simultaneous formation of lanthionine.[44] The formation of decomposition products during treatment of cotton with sodium carbonate may affect the vat dyeing. Their formation may be followed by measuring the changes in oxidation-reduction potential under the varying conditions of temperature, pressure, agitation, and presence or absence of oxygen. High leuco-potentials are in general correlated with resistance to alkali.[45]

Repeated exposure of cotton and regenerated celluloses to boiling aqueous alkalies is harmful. At equivalent Na_2O concentration caustic soda and sodium metasilicate are more destructive than the carbonate.[46]

Large quantities of soda take part in the recovery processes in wood-pulp residual liquor. Waste sulphite liquor is treated by addition of a part of an alkaline liquor containing sodium carbonate and sulphide from the subsequent furnace reduction of the non-acid mixed liquors, giving a melt containing sodium carbonate and sulphide.[47](See Manufacture of Sodium Carbonate: Other Methods).

Bleachable pulps with low lignin content are prepared by pulping wood for 2–5 hr. at 125–175°C., 800 lb./sq. in. partial oxygen pressure and pH 7–9 with a complex alkaline solution based on bicarbonate and borax with benzoate, thiosulphate, phenolate and disodium phosphate, 300 parts requiring approximately 150 parts of bicarbonate.[48]

Some 2–2·5% of the total production of soda ash is used in the textile industries, and about double that quantity of caustic soda, which of course derives from soda ash initially; half that amount is consumed in the manufacture of rayon.[49]

In dyeing cellulose acetate and other materials vat colour printing pastes may be prepared as oil-in-water emulsions in which sodium carbonate is a necessary water-soluble electrolyte.[95,96]

Testing standards for sodium carbonate and the products of the textile industry are given in a lengthy publication of the American Society for Testing Materials.[50]

Sodium carbonate in 20-40% concentration is an active ingredient in a cellulose cooking liquor. If dry sawdust is cooked at about 180°C. and some 100 lb./sq. in. steam pressure, the resulting liquor is reddish black and contains larger quantities of lignin and volatile acid than does the residual wood, which is lighter in colour and softer than a water-cooked product. The pentosans normally held by the cellulose in a stable association are not removed, so that larger quantities of cellulose are retained. The α-cellulose content, however, is lower than in the water cook.[51]

Corrosion.

Sodium carbonate has been found profitable in protection against corrosion either alone or in mixture with other salts, particularly chromates, dichromates, phosphates and nitrates.[52] The following are examples:- protection of automobile radiators (1–3%)[53] and of refrigerating ammonia condensers;[54] (with dichromate) protection of steel against brine drippings from refrigerated cars on railways;[55] the depression of iron corrosion by surface-active agents;[56] treatment of diesel-engine coolant water (equal parts of potassium chromate and soda);[57] the presence of carbonate or bicarbonate reduces the amount of chromate otherwise needed for protection.[58]

Steel surgical instruments treated with a boiling 0·4% aqueous solution of '*Passivin*' (a mixture of carbonate and nitrite) are resistant to corrosion for at least a week.[59]

For the mechanism of protection and inhibition see Electrical Properties.

Many ternary alloys have been made for dental purposes (Sn 82–93, Bi 2–10, Sb 3–8%; some may contain Sn, Bi, Cd, Ag); these are extremely corrosion resistant to 1% bicarbonate and 1% carbonate.[60]

On the other hand blistering and tuberculation of steel and cast iron is at a maximum in a solution containing 20 p.p.m. of sodium bicarbonate and 16 p.p.m. of calcium sulphate;[61] the corrosion by leaching solutions from alumina production is largely due to the bicarbonates of sodium or potassium and to sodium sulphate, helped by the presence of air. Grey cast iron is however stable to bicarbonates.[62]

In high-pressure boilers the water after treatment may still contain sodium bicarbonate, which dissolves the calcium and magnesium incrustations, increases the hardness of the water, and corrodes the boilers. Oil wells producing relatively small amounts of water may be treated by injecting sodium bicarbonate either as an aqueous solution or in the form of cylindrical pellets bound by ethyl silicate, calcined magnesia and magnesium chloride solution, or melamine resin and magnesium chloride solution. The pellets are compressed at about 5000 lb./sq. in.; they neutralize the acidity without plugging the formation.[63] Corrosion in oil and gas wells can also be met by intermittent injection of alkaline solutions (2·5 lb. of washing soda in 30 gallons of water every million cubic feet of produced gas).[64]

Detergency.

Soda alone has considerable detergent action; its addition to synthetic detergents increases their action to a maximum at pH = 10·7.[65] With natural soaps (palmitate, stearate) a large amount of carbonate raises the surface tension and reduces the emulsifying effect, and is therefore not desirable in such cases.[66] In softening water trisodium phosphate is preferable to sodium carbonate[67] which does not remove calcium oleate from fabrics and will not prevent soap losses in laundering with hard water.[68] The quantities of soda required to transform half the calcium oleate into a sodium soap may be as much as 200 times the calculated value at dilutions of the order of 2 g. oleate per litre of water.[69] The calcium-sequestering action of detergents containing polyphosphates is reduced by the presence of alkalis such as sodium carbonate, which contain calcium-precipitating ions. The highly adverse effect increases with the concentration of the alkali.[130]

Another estimate of detergent powers gives $Na_2SiO_4 > NaOH > Na_3PO_4 > Na_2CO_3$. The pH values of these substances for optimum detergency are respectively 10·8, 10·6, 10·1–10·2, and 10·1–10·2.[70,71] The relative efficacy of alkalis and detergents in cleaning milk from glass slides under stated experimental conditions is as follows (at equivalent alkalinity):-[72]

0·20%	NaOH	96	0·05%	*'Santomerse'*	94
0·53%	$Na_2SiO_3,5H_2O$	98	0·2%	*'Teepol 610'*	95
0·95%	$Na_3PO_4,12H_2O$	91	0·02%	sodium oleate	98
0·27%	Na_2CO_3	70	0·01%	*'Santomerse'* with 0·2% Na_2CO_3.	95

A mixture of sesquicarbonate, non-ionic detergent and sodium tripolyphosphate (200:20:100) is recommended for ampoule cleansing.[73]

There are many patent specifications for mixtures of soda with sodium sulphate or silicate to produce cleansing compositions, and for the technical processes involved. The problem is to effect a very partial hydration of the soda ash either directly or from the bicarbonate without caking. This may be done in towers or chambers, or on conveyor belts; jets of compressed air, and sprays of water or steam and of sulphate, silicate, or soap solutions are introduced as necessary.[74] Stabilized washing-soda compositions which overcome the instability of the decahydrate may contain 2–6% by weight of the calcined monohydrate and a synthetic detergent such as sodium lauryl sulphonate (2–6%).[75]

Washing can be accomplished with soda plus water glass without fatty-acid soaps. The efficient removal of 'soil' is a question of pH and temperature; this is not the whole story since the soil must also be retained in the washing solution through the presence of an anion-active substance such as the silicate.[76,77] The so-called 'bleaching sodas' are mainly mixtures of carbonate and 6–12% of water glass. They have the advantage of greater softening action and also precipitate iron salts; they are superior to sodium carbonate in cleansing power and cause less damage to the strength and colour of fabrics. The combination apparently does not corrode aluminium or the other metals used in washing machines.[78]

A very dilute soap is mainly crystalloid. In more concentrated solutions (0·1%), which are more effective cleansers, a reasonable part of the soap is present as colloidal micelles. The effect of a soap builder is to increase this portion and also to neutralize acidic ingredients commonly present in dirt. The pH of a 'neutral' commercial soap is 10·2 in 0·1% solution.

The compounds added as binders or 'builders' have total alkalinities slightly different in order from the available alkalinities. For rational comparison pH must be translated into $[OH^-]$. Because of the necessity of neutralizing acid dirt, something in the nature of a buffered builder is necessary; this excludes caustic soda.[79]

Soda ash has many advantages as a soap binder; it is low-priced, easily obtainable, blends well, is compatible with other alkalis and fillers, has usually no detrimental effect on colour, and does not produce rancidity; the soaps dissolve easily giving good lathers. The tendency of soaps containing soda ash to be moist is inhibited by reducing the water content or incorporating sodium silicate.[80,81]

Sodium carbonate in a soap cake tends to migrate to the surface. The effect is of course intensified in thin layers. If, however, free fat is present this is gradually saponified and outside layers of such soap show a practical absence of sodium hydroxide and carbonate after a year or more.[82]

The disadvantage of sodium carbonate is that it tends to increase the iron-binding properties of washing powders and so reduce whiteness.[83] The pH of these mixtures is governed largely by the sodium carbonate and is represented by the equation: $pH = 10{\cdot}79 + 0{\cdot}49 \log g$, where g is the concentration of the detergent in g./l.,[84] pH increasing with rise in temperature from 16 to 85°C. For 'modified soda' (Na_2CO_3 41, $NaHCO_3$ 45, H_2O 14%) or sesquicarbonate the maximum pH occurs at about 0·6 g./l. and is 10·0 at 25°C., 9·85 at 40°C., and 9·68 at 60°C.; it decreases the pH of soap solutions except at 60°C. and higher temperatures;[85] bicarbonate alone is of little aid to soap.[86] Soil removal and whiteness-retention are independent; in detergent systems composed of a sodium alkylaryl sulphonate with sodium carbonate, the partial substitution of alkali by sodium carboxymethylcellulose yields large increases in detergency; at 0·25–0·5% detergent concentration the relative carbon-soil-removal values are increased about 67% and the whiteness retention values about 900%.[87] It is interesting to note that during the seasoning by natural drying of soaps which may contain both carbonate and chloride, sodium carbonate migrates to the surface of the sample and sodium chloride to the centre.[88]

Many commercial formulae are available for mixtures of sodium carbonate with other substances having some specific cleansing purpose, such as sodium hypochlorite,[89] hydrogen peroxide as $Na_2CO_3,H_2O,1{\cdot}5H_2O_2$;[90] or mild and refractory clays. The carbonate (and bicarbonate) play a great part in scouring oils from wool; in this they are associated with various alcohols, emulsifiers and soaps.[91-93] Sodium carbonate is used in the refining of crude fatty oils; the soap stocks from the carbonate and caustic refining are different in that the carbonate treatment results in some complex with phosphatides which does not decompose readily; on extraction with petroleum ether it yields a semi-solid mass high in phosphorus content, while the caustic soda soap stock yields an oil low in phosphorus.[94]

Fire-Proofing and Retarding.

Sodium carbonate has some fireproofing qualities; incorporated in insulating board and similar materials it is effective, but requires a neutral size.[97] It may be used as a low melting-point combustion regulator in combustible tablets and pastilles.[98]

Sodium bicarbonate is of importance both in flame proofing and as an extinguisher. The problem of explosions and fires in mills handling combustible powders such as flour, cocoa, sugar, cork, etc., was intensified during the Second World War; high-explosive bombs shake off accumulated dust from walls, ceilings and machinery and lead to a secondary explosion usually followed by fire. Propagation of the dust explosion is inhibited by packets of non-combustible dusts (sodium bicarbonate and limestone) placed in likely positions in the building.[99-101] The bicarbonate gives excellent results when used on fires due to inflammable liquids (ether), gases (diborane)[102] and electrical equipment.[103] It can be sprayed from a dry extinguisher by gaseous carbon dioxide under pressure,[104] and with enhanced properties by admixture with about 0·5% by weight of silica aerogel which promotes dispersion of the bicarbonate and removes surface moisture from it.[105] Dry compositions based on the compound are also rendered free-flowing and non-caking by the addition of 1–2% of powdered mica and 1–2% of a water-insoluble metallic soap such as magnesium or zinc stearate.[106] The most effective pure powder extinguisher in small-scale experiments is potassium oxalate, but a mixture of 30% oxalate with 70% sodium bicarbonate is even better.[108] In the flameproofing of textiles it may be incorporated in emulsions containing halomethylated phosphates; with appropriate treatment cotton fabric dipped in the emulsion produces a cloth which does not lose its flameproofing after eight washes.[107] The use of sodium bicarbonate alone in preliminary treatment has advantages; for example, it may be dusted on baled cotton as a fire-retardant without adverse effects on manufacturing or finishing.[109]

Several investigations have explored the mechanism of fire-proofing by the bicarbonate. When used in dry extinguishers the powder cloud has considerable heat-absorbing ability partly accounting for its extinguishing properties; it therefore serves as a screen to shield the fire fighter, and the liberation of carbon dioxide during the decomposition of the bicarbonate aids in smothering the fire.[104]

The use of specially treated dry bicarbonate has proved successful in the extinguishing of bad oil-well fires where foam, water, and carbon dioxide have failed.[110] The flame-retarding role is an expression of the same reaction mechanism as the smouldering which replaces the flame. In the pyrolysis of cellulose either impregnated with bicarbonate or mixed with the dry powder, the tar/char ratio has been determined and in each case there is a decrease in tar production and an increase in char. Caustic alkalis have a similar effect and it is suggested that it is the degrading action of sodium hydroxide produced by the heating of bicarbonate in the presence of water vapour which is responsible for the fire-retarding effect when bicarbonate is applied as an impregnation. There is a pre-flame break-up of the cellulose molecule, and the amount of tarry distillate is reduced, so that the source of exothermic reaction is removed.[111] Measurements of the total gas volume and its composition with the yield of charcoal during pyrolysis of cellulose (0·5 g. samples heated at 480°C. for 1 hr.) suggest that the organic vapours produced are important in the combustion of cellulose, and confirm that the principal effect of bicarbonate and other fire-resistant chemicals is to prevent the emission of these vapours.[112] It may of course be remarked that no inconsiderable amount of the bicarbonate is used with acids - real or potential - in the liquid-expulsion type of extinguisher, with or without the addition of foaming agents.[113]

It should be noted however that the ignition temperature of active carbon is lowered by the addition of salts in the order $KOH > NaOH > K_2CO_3 > Na_2CO_3 > NaHCO_3 > Ca(OH)_2$.[114]

Food.

Alginates.

Seaweed stems peeled, crushed and washed are bleached with hypochlorite and then treated with soda solution to yield sodium alginate. If the weed has been dried it is soaked and washed, and treated with aluminium sulphate solution followed by sodium carbonate to soften the cellulose.[115]

Butter.

If prepared for storage butter should be salted with a mixture of disodium hydrogen phosphate and sodium carbonate (its equivalent in the Swedish trade is the proprietary '*SMR*'); the pH is controlled at 6–7. This is not used in butter for direct consumption unless there is a risk of oiliness developing (July–October).[116]

Sugar.

Light soda-ash, partly replacing lime, is used in cane-juice clarification,[117] and in the treatment of beet juice during defecation;[118] it has however a high melassigenic coefficient and may produce slow crystallization and difficult purging.[296]

The addition of 2·5 g. per thousand g. of brine in salting hams for early consumption increases the development of microbial flora which favour the formation of nitrite from nitrate and so yields a product of good colour.[131]

Baking Powders and Food Stuffs.

It has been recently shown that increasing the proportion of bicarbonate in baking powders leads to decreased retention of thiamine in baking; if the soda content is largely in excess of requirements, riboflavin may not be retained and the quality of the goods decreases.[119] The excess may be determined by Tillmann's procedure.[120] Tables showing the efficacy of the bicarbonate with different acids in gas production are available.[121]

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A summary has been made of the development of leavening agents for baked products, in which the approximate compositions of tartrate, phosphate and combination powders are described, together with the methods of analysis. A new leavening agent has been found in acetonedicarboxylic acid.[122]

Table salt may be prepared by treating small crystals of sodium chloride with sodium carbonate to precipitate the calcium salts, thoroughly mixing and drying.[123]

Glass Manufacture.

The glass industry requires a dense soda: one method of manufacture is to form a slurry of monohydrate crystals in a saturated solution, to raise the temperature above the transition point between the anhydrous salt and the monohydrate, and to recover the deposited anhydrous product.[124] The properties of various types of sodium carbonate and their control for the needs of the glass industry have been discussed,[125] as have been the weight used and the grain size in relation to batching difficulties.[126] The course and rate of the reaction between sodium carbonate and silica are considered in the section on Kinetics. It is stated that the reactions in binary mixtures of soda ash with silica or cullet are not appreciably affected by the grain size of the materials and are complete after 3 hr. at 900°C. In the ternary mixture of soda ash, calcium carbonate and silica the reactions are accelerated by the addition of cullet, being most rapid with cullet of 0·15 mm. grain size and below and least with large grain sizes, e.g. 1·00–1·50 mm.[127]

The merits and demerits of soda and of sodium sulphate in glass manufacture have been fully discussed.[128,129]

A number of thermochemical and microscopical analyses have been made of the reactions between soda, lime and silica and of the effect on this reaction of the introduction of such impurities as sodium chloride.[132] In laboratory experiments it has been shown that Solvay soda reacts more vigorously than pure soda, and various kinds of sand show considerable difference in their behaviour towards Solvay soda. The effects are the combined results of varying chemical and mineralogical composition and of grain size or reacting surface.[133]

Light ash batches show a strong tendency to balling up and subsequent melting down becomes troublesome; the dense ash seems to result in faster melting. The best form is a granulated ash with particles a little less in diameter than the average grains of sand and limestone.[126]

Metallurgy.

Iron and Steel.

The cementation reaction is largely $3Fe + 2CO \rightarrow Fe_3C + CO_2$ followed by $CO_2 + C \rightarrow 2CO$, the latter reaction taking place only in the absence of water; otherwise carbon dioxide and hydrogen result. To retain and increase the carbon dioxide content 15–30% of soda ash may be added to the cementation mixture, the decomposition at high temperature being responsible. The exhausted mixture may be regenerated by carbonating the sodium oxide by carbon dioxide from the air.[134]

Soda ash is consumed in many of the mixtures and for case-hardening, carburizing and carbonitridation. As a liquid carburizer pure molten sodium carbonate containing 0·5% of sodium cyanide gives a case 0·002 in. deep at 850°C.[135]

The solubility of carbon in case iron at 1500°C. is increased by soaking the coke in saturated aqueous sodium carbonate.[136] Case-hardening powders may be prepared by soaking grained charcoal with sodium carbonate solution to give 2·5–3% soda content,[137] or the carbonate may be added as a layer on top of the charcoal;[138] in the first method the carbonate acts as an energizer to an upper layer or sprinkling of such mixtures as sodium and barium formates. The activation by carbonates and oxides depends on the transforming of the oxygen content to carbon monoxide, which is the effective carburization gas, and the conversion of the carbonate into the metal and carbon monoxide with formation of alkali-metal carbide. Barium carbonate is less prone to give excess carbide than soda.[139] A fused-salt bath containing 25–75% of sodium carbonate and 75–25% of sodium chloride with 0·1 to 10% of finely divided carbon can be used for simultaneous carburizing and nitriding if ammonia and an oxygen-containing gas such as carbon monoxide, carbon dioxide or nitrous oxide is passed through the melt. The presence of at least 25% of potassium carbonate appeared to induce more active carburization than soda alone.[140]

Sodium bicarbonate acts as an accelerator during the first hour of the process, but with its decomposition its activity falls to zero in the third hour.[141] To obtain the same result with a pack a mixture of 20% of sodium cyanide, 10–20% of soda ash and the remainder charcoal is recommended.[142] Alternatively charcoal grains (10kg., 1·5 cm. diameter) can be sprayed with solutions of 3kg. of barium hydroxide octahydrate, 1kg. of soda ash and 0·8 kg. of calcium cyanide, and then dried.[143] Malleable cast iron may be graphited by a first treatment at 950°C. in a bath of mixed chlorides (e.g. of barium and potassium), and a second treatment in a bath of sodium carbonate with chlorides and a phosphate at 700°C. while an electric current is passed through the bath. The heating cycle is thus reduced from 145 to 13hr.[144] A study of the suitability of various promoters for mild carburization has been made. The sodium carbonate–lime system is excellent for mild carburization.[145] If high-carbon steels are heated in a salt bath the steels are inevitably decarburized and corroded. The addition of soda to a mixed $BaCl_2$–NaCl bath accelerates the corrosion but does not affect the decarburization.[146] A high degree of carburization is obtained by submerging steel for a few hours in a melt of sodium carbonate and titanium dioxide, which forms a corrosion-resistant film. The process improves as the temperature rises; the mixture easily penetrates and fills the pores of the metal and produces a stronger steel. A wire originally containing 0·035% of carbon was left in a bath containing 20% of TiO_2 and 80% of Na_2CO_3 for 2hr. at 950°C.; after treatment it contained 0·44% of carbon and its bending strength was greater than that obtained by the usual commercial bath of Na_2CO_3 60, $BaCO_3$ 20, NaCl 10 and C 10%.[147] A carbonitriding bath composed principally of sodium cyanide is said by some workers to give a thicker carburized layer when about 50mol.-% of barium chloride or carbonate are added rather than sodium carbonate; the melting point is also lower, as is the viscosity.[148]

The desulphurization and dephosphorization of molten iron is obtained by use of soda ash; sulphur reduction of 75 to 80% in cupola and pig iron may be obtained by adding 20–45 lb./ton to the metal. Reductions in phosphorus of up to 20% are obtainable at the same time. A full account of the process giving descriptions of methods, temperatures, and analysis is available. The greatest desulphurization efficiency is obtained by adding blocks of soda ash in amounts 'prescribed by experience' to the point where the stream of metal from the cupola enters the ladle; the spent slag and refined metal are drawn off at a point as far from the molten stream as possible.[149]

The fundamental reaction studied by Berthier in 1830 is $FeS + Na_2CO_3 + 2C = Na_2S + Fe + 3CO$. The sodium carbonate has been shown to produce metallic sodium, which reacts violently with oxygen and sulphur compounds. If the carbonate is allowed to mix with the cupola slag, it reacts preferentially and renders sulphur soluble again.[150]

Double treatment and pouring increases the removal of sulphur; a ladle lining poor in silica should be used. Increased dephosphorization (35%)

can be obtained by using a mixture of mill scale (Fe_2O_3) and soda; this increases the silica removal but lowers desulphurization. Lime and fluorspar added to the soda increase the removal of sulphur and phosphorus. Ladle charges of 5 tons of metal are readily treated, but regular patching of the linings is a necessity.[151] Under favourable conditions 85% of the phosphorus present in a pig iron containing 1·34% of phosphorus has been removed. With the exception of calcium nitride no markedly better desulphurizing agent than sodium carbonate has been found.[152,153] Briquetting, although increasing the ease of handling, gives a slower-melting charge; moreover, the carbonate is partly converted into bicarbonate on air storage, with a resultant too rapid liberation of too much carbon dioxide.[154] Several patents and papers refer to the use of sintered masses of soda ash, pig-iron powder and rolling scale.[155] The desulphurization effectiveness of soda depends greatly on the soda concentration, and is much less at higher temperatures.[156] It is attributable to the formation of ferrous sulphide which is almost insoluble in molten iron and stable at temperatures over 1400°C. An account of the introduction of soda slag in Germany during the last war is available. The elimination of difficulties due to loss of iron or contamination with the slag, the recovery of iron from the slag and its use in the glass industry are also considered.[157]

A typical example of the application of the process is in the production of low-sulphur rimming steel when blast-furnace iron containing 0·030 to 0·27% of sulphur is poured into 80-ton ladles containing soda ash at a tapping temperature of 1580°C. The desulphurizing process is customarily repeated to ensure a low sulphur content (below 0·05%).[158]

The process of desulphurization with soda is efficient and economical owing to the small solubility of ferrous sulphide in iron and its comparatively high solubility in the dross rich in sodium sulphide, the partition coefficient varying from 91 to 4800. The adverse effect of a high silica content is shown by a reduction to 28–130.[159] 0·5% soda ash in the ladle into which cupola iron is poured not only reduces the sulphur content but improves separation of the metal from the slag and reduces porosity.[160] It also purifies cast iron from slag inclusions thereby reducing waste; the iron is also rendered more fluid so that a lower casting temperature can be used.[161]

A recommended dephosphorizing agent is made by treating soda ash with an equimolecular amount of fine-grained calcium carbonate in aqueous suspension at about 40–60°C.[162] Molten steel may be dephosphorized by heating with a solid mixture of caustic soda (27·5%) and haematite (62·5%) or alternatively with 24 parts of calcium hydroxide, 36 of sodium carbonate and 40 of haematite.[163]

The use of sodium carbonate in these processes makes demands upon the refractories. Well burned, dense, hard firebrick is best, and tight joints between the bricks are essential.[164]

Smelting.

Sodium carbonate with a reducing agent finds frequent use in the isolation of many metals. For example, a titaniferous magnitite showing about TiO_2 18·8, Fe_2O_3 57·5% is ground, mixed with coke and light soda ash, and roasted at 1050–1080°C.; the iron is obtained as a sponge, with titanium oxide retained in the slag.[165] Some titaniferous magnetites contain vanadium. If the ore is crushed, mixed with soda ash, sintered and treated in a blast furnace at 1450°C. the vanadium collects in the metal. The iron and slag, which contains the bulk of the titanium, are separated, the metal going to a Bessemer converter. The vanadium then appears in the slag.[166]

The presence of sodium carbonate in a carbonaceous reducing mixture markedly increases the rate of reduction of iron ores, the effect being greatest at 900°C.[167] The simultaneous recovery of metals and sulphur from metallic sulphides is achieved through carbon and soda ash in an atmosphere of carbon monoxide. Calcium fluoride or carbide used as a flux gives a fluid sodium or calcium sulphide slag, which when treated with steam and carbon dioxide allows the recovery of sulphur and alkali. Lead sulphide may be smelted in this way with soda ash and charcoal.[168]

Alloying elements may be added to molten iron and steel when made up into exothermic mixtures such as potassium perchlorate, sodium carbonate and ferrosilicon, or silicon with alloying elements. Rapid solution is achieved without lowering the temperature.[169] The activating properties of sodium carbonate make it especially useful as a binding agent in 'clumping' mixtures of iron sand, reducer and clay for smelting.[170]

It appears that cast iron may be soldered with a mixture of iron powder with 6–10% soda ash.[171]

Copper and Lead.

Copper is recovered from lead blast furnace bullion which is drossed with sulphur to remove the copper. In the soda-mat process 5•5% of soda ash and 1% of fine coke are charged with the dross in a furnace with a semi-cylindrical hearth 4 ft. deep.[172] The slag resulting from the treatment of arsenical molten copper with soda ash and quicklime is pulverized and brought into contact once more with aqueous 2–15% sodium carbonate at 180°F.; the arsenic dissolves and leaves the copper-containing residue.[173]

The smelting of lead sulphide to the metal can be achieved in one phase. In the presence of carbon the lead sulphide reacts with a metallic oxide, preferably zinc or ferrous oxide, an alkali sulphide and sodium carbonate at 1290–1470° F. in the stoicheiometric proportions represented by the equations: $PbS + ZnO + Na_2S + C \rightleftharpoons Pb + ZnS + Na_2S + CO$; and $PbS + Na_2CO_3 + 2C \rightleftharpoons Pb + Na_2S + 3CO$. The metallic lead yield is 97–99% and is 99•9% pure.[174] The agglomeration of ores and slags is often an important preliminary process. They can be nodulized by moistening a finely divided mixture of the material with soda ash and agitating at 35–100°C. until nodules are formed, and then burning at 1000°C. The process is suitable for water glass, bauxite, and cryolite, and the treatment of ores and slags of uranium, tungsten, vanadium etc.[175]

Soda ash can be used as a binder to lock up loose water in nodulized mixtures such as caustic soda with sodium silicate.[176]

Uranium.

In contact with aqueous solutions containing carbonate and oxygen, U_3O_8 in pitchblende is further oxidized to the sexavalent state and dissolves as a complex ion, $[UO_2(CO_3)_3]^{4-}$. This reaction forms the basis of the pressure-carbonate-leaching of uranium ores; it depends on the high solubility of the alkali salts of the complex. The accumulation of hydroxyl ion produced in the reaction may cause reprecipitation of uranium as a sodium uranate, and it is therefore desirable to have bicarbonate ions present in addition to the carbonate. The stoicheiometric relationships indicate that the minimum requirements of the solution of 1 part of U_3O_8 are O_2 0•02, Na_2CO_3 0•38 and $NaHCO_3$ 0•60 parts, the leaching being carried out at 100°C. by a solution containing 50 g./l. of Na_2CO_3 and at an oxygen pressure of 2 atm. An extraction of 92–99% is effected, the rate of leaching being proportional to the square root of the pressure of oxygen. The activation energy (9700 g.-cal./mole for an ore containing 0•41% of U_3O_8) corresponds to an increase in the rate of about 50% for every 10° rise in temperature. The best results are obtained between 80° and 115°C., since at higher temperatures excessive amounts of silica are dissolved.[177] An improved method for precipitating uranium, especially from low-grade carbonate solutions, depends on the fact that quadrivalent uranium, unlike the sexavalent ion, does not form a carbonate complex and is completely insoluble in carbonate solutions. By treating the solution with commercial hydrogen under pressure in the presence of a nickel powder catalyst the reduction of the uranium can be made to proceed at a convenient rate at moderate temperatures (120°C.) and hydrogen pressures (8 atm.). Most impurities do not interfere; residual uranium is less than 0·01 g./l. of U_3O_8. Each lb. of the oxide requires 0·007 lb. of hydrogen and 0·75 lb. of sodium carbonate. The solutions may be recycled.[178]

Tungsten.

Two methods of extracting tungsten trioxide, WO_3, from scheelite, $CaWO_4$, have recently been examined. They are based on sodium carbonate, not on the conventional hydrochloric acid, extraction. A flotation concentrate containing WO_3 28·5, SiO_2 7·54 and CaO 31·75% was used. A mixture of ore 2, Na_2CO_3 2, and wood charcoal 0·5 parts was roasted. at 750°C. for 2 hr., giving the best extraction, 97·46%. If charcoal was not used the extraction was 91·48%. The amount of carbonate required is 7·7 times the calculated amount based on the equation $CaWO_4 + Na_2CO_3 + C = Na_2WO_4 + CaO + 2CO$. The other is the autoclave-soda method by which soda reacts with scheelite under high pressure to form hardly soluble calcium carbonate; 500 g. of ore per l. of 20% aqueous sodium carbonate was heated to 190°C. under 13 atm. for 4 hr. with stirring at 45 r.p.m. This gave 96·5% yield of trioxide.[179] Most deposits of scheelite now worked are low-grade; the above autoclave process is worked at Salt Lake, Utah. The flotation concentrates are blended and pulped with soda solution to give a slurry containing 7% of WO_3. The rate of conversion of $CaWO_4$ to Na_2WO_4 decreases with increasing concentration of the latter and limits the process to the low-grade material. Impurities are removed by pressure filtration and the sodium tungstate converted to a synthetic scheelite with lime.[180]

The purification of some metals is achieved through soda ash. Metals in porous or powder form immediately after reduction from the ores (e.g., magnesite or iron oxide) may be brought into contact below their melting points with a molten flux of fusion mixture which does not attack the metal but dissolves impurities. The metal is separated and washed.[181] Fluxing agents for welding and hard soldering heavy metals may be made from sodium carbonate and pentaborate ($3Na_2CO_3 + 2Na_2O,5B_2O_3 \rightarrow 5Na_2O,2B_2O_3 + 3CO_2$); the mixture has the advantage of not swelling on heating.[182] Brass and bronze may be purified by adding them to molten soda ash above the melting point of the metal, which melts and is purified as it drops through; some 13 metric tons of red brass may be treated by 1½ tons of soda ash at 2200°F. A process of desulphurization occurs and the sulphur content is reduced from 0·54 to 0·11%.[183] Complicated prescriptions have been devised for compositions of heavy mixtures to be dropped as pastilles into molten metals for purification; for aluminium and its alloys the formula includes sodium carbonate with lead, lead chloride, potassium nitrate and chloride, sodium sulphate, chloride, and fluoride and cryolite.[184] Oxidized heat- and corrosion-resistant metals such as high nickel, chromium, copper, or molybdenum alloys may be simultaneously annealed and descaled with practically no loss of base metal by immersing the oxidized metal in a salt bath of 20–80% sodium fluoride, the rest carbonate, for at least 2 min. at 1500–2000°F.[185]

Titanium.

The reducing alkaline fusion of ilmenite, FeO,TiO_2, produces slags readily soluble in sulphuric acid to give titanous sulphate; they contain mixed titanates derived from $3TiO_2,Na_2O$, the maximum solubility of titanium in the sodium slags being 80%. Sodium carbonate has the important advantages of lowest temperature of slag formation (1200°C.), widest utilizable temperature range (1200–1380°C.) and highest degree of solubility of titanium (80%).[186]

Graphite.

The impurities in earthy and scaly samples are not easily removed by oil flotation; fusion with soda ash or its mixture with limestone powder is better.[187]

Antimony.

Tellurium can be removed from metallic antimony by mixing soda or caustic alkali with the molten metal and passing a reducing gas such as natural or coal gas through the mixture. A slag is formed containing tellurium and is separated by skimming. Tellurium volatalizes continuously from the slag during the process so no undesirably high concentration is obtained in the slag. About 3 lb. of antimony are lost per lb. of tellurium removed.[188]

Sodium Carbonate in the Production and Recovery of Metallic Salts and Compounds

Potassium.

Mention should be made of the many ways in which soda assists in the recovery of potash from natural sources, particularly in the solution mining of potassium compounds. For example, soda may be added to the brine to raise the pH to 8–10 in order to eliminate the interference of magnesium or sulphate compounds: the solubility of these ions is repressed and potassium compounds are dissolved at a correspondingly higher rate.[225]

Magnesium.

After addition of chalk and decantation, sea water is treated with carbon dioxide to remove calcium; the magnesium salts are precipitated from the warm, clear residual solution as a basic carbonate by sodium carbonate.[189]

Barium.

A U.S. patent describes the procedure for converting barite, $BaSO_4$, to barium carbonate by boiling in soda liquor. 20 parts, ground to about 200 mesh, are added slowly to the boiling carbonate ($22Na_2CO_3$:$50H_2O$) and the heating continued for 10–15 min. A second portion of boiling carbonate liquor ($10Na_2CO_3$:$25H_2O$) is added slowly to the first mixture and the heating continued for an additional 10–15 min. The supernatant liquid is drawn off while hot and the solids (about 50% $BaCO_3$) are filtered and used for the production of barium salts.[191]

Calcium.

The production of $CaCO_3,6H_2O$ is described in a British patent. It is precipitated at 10–20°C. by stirring together 0·1 N. solutions of calcium chloride and sodium carbonate containing 50 p.p.m. of glassy sodium polyphosphate (Na_2O/P_2O_5 molar ratio 1·12:1). The precipitate is filtered and dried; it has a high porosity and specific surface area and is useful as a paint or rubber filler.[192] Extra light calcium carbonate can be obtained by adding portions of aqueous calcium hydrosulphide ($Ca(SH)_2$) to stirred aqueous sodium carbonate. The sodium hydrosulphide solution obtained is treated with carbon dioxide to regenerate sodium carbonate, and the hydrogen sulphide produced is passed into an aqueous suspension of lime to give $Ca(SH)_2$. If the solution of the latter is added to the soda in several portions of diminishing size, the size of the calcium carbonate crystals is reduced. All the operations are best carried out in an inert atmosphere.[193]

Chromium.

Large quantities of wash waters containing low concentrations of toxic dichromate from plating works are treated with sulphur dioxide and sodium carbonate solution; Cr^{6+} is reduced to Cr^{3+} and the latter is precipitated, the water remaining essentially free from contaminants.[190] Ground chromite mixed with the necessary amount of soda ash may be compressed into bricks and fired. The hot bricks are leached with water and acids to give dichromate.[194]

The oxidative fusion of chromite with soda is aided by the addition of 40% of ferric oxide instead of the usual lime; better·leaching of the chromate is claimed. The ferric oxide can be recycled.[195]

Aluminium.

The commercial production of aluminium from bauxites has provoked considerable research, particularly by Japanese and Russian workers, with the object of replacing caustic soda wholly or partly by soda ash in a so-called soda-lime process. In one apparently successful attempt a finely ground bauxite containing 13–15% of SiO_2 is heated with limestone in a rotary furnace and lixiviated with soda solution. Nepheline (approximately $(Na,K)AlSiO_4$) is a waste product from the flotation of apatite; it may contain up to 20% of basic material and 30% of Al_2O_3, the rest being silica. If this is treated as above, the limestone–silica slime is removed and used for cement; the sodium and potassium aluminates are freed from silica and treated with carbon dioxide, so that nepheline yields alumina, soda, potassium carbonate and cement.[196,197] The addition of 4% of soda to a mixture of calcium carbonate and nepheline reduces the time required for sintering to 1hr. at 1000°C., yielding over 90% of the alumina on leaching.[198] A number of crystalline calcium aluminates have been synthesized and examined for their extraction properties on fusion with soda ash. Thus CaO,Al_2O_3 is best treated by a mixture of 1·2moles of Na_2CO_3 and 0·4moles of NaOH per mole of Al_2O_3. $3CaO,5Al_2O_3$ and $5CaO,3Al_2O_3$ were also examined.[199] A fused mass of aluminous clay and limestone was investigated; to ensure a good extraction of alumina with sodium carbonate solution requires the silica content of the calcium aluminate slag to be less than 8%. The pure aluminate $3CaO,5Al_2O_3$ shows the best extractability, 93–96% of the alumina in one hour.[200] Mixtures of soda ash and lime with $1Al_2O_3{:}2SiO_2$ were calcined at 800–1300°C., pulverized, and extracted with hot water. With 4 or 5 moles of soda a maximum extraction of 99% of the alumina and 95% of the soda was effected. Many other mixtures were examined; it is inferred that the main compounds formed by the calcination are $3Na_2O,Al_2O_3$ and CaO,SiO_2.[201] The Deville–Pechiney method, in which lime is not used, gives much the same results as the soda-lime method when the silica content is low.

The production of alumina by the sintering process in the rotary kiln has been examined for (i) the mixing ratio of soda and lime and the sintering temperature and (ii) the behaviour of natural aluminium compounds and synthesized calcium compounds with sodium carbonate and sodium aluminate.[202]

Pilot-plant runs have shown that alumina and soda in anorthoclase, $(Na,K)AlSi_3O_8$, can be extracted and recovered by the lime–soda sinter process. Liquors containing 95g./l. of alumina can be produced over a range of $Na_2O{:}Al_2O_3$ ratios; they can be desilicated and carbonated to yield a high-grade alumina trihydrate.[203] The soda is of course largely recovered, either as monohydrate by evaporation or decahydrate by cooling. After dehydration 98–99%Na_2CO_3 is obtained, the major impurity being alumina from retained mother liquor.[204]

A German patent exists for the breakdown of aluminium phosphate by calcining with lime and soda proportioned to supply 2 moles of alkaline-earth oxide and one of alkali-metal oxide for each mole of phosphorus pentoxide present, and adding at the same time one additional mole of alkali-metal oxide for each mole of alumina. Alkali metal aluminate and di-alkaline earth phosphate are formed. The product is leached with water.[205]

The concrete vessels used in the alkali extraction of aluminium are rendered passive by preliminary treatment with soda solution which also removes soluble silica.[206]

Cyanides.

Sodium cyanide may be prepared in 90% yield by a patented process involving passing a mixture of soda ash, coke and ferric oxide through a chamber heated to 950–1000°C. into which is passing a stream of nitrogen. The carbon monoxide produced and excess nitrogen are recycled.[207]

The solid reactant, finely dispersed in coke-oven or town gas, may be injected axially as an annular stream inside a reaction chamber raised to the required temperature. The reaction mixture may be enveloped by injected preheated gas. This is proposed as a general method for carrying out endothermic reactions between solid and gaseous reactants.[208]

Sodium ferrocyanide may be prepared from a molten mixture of calcined soda and wood charcoal (2:1) by adding nitrogeneous waste and scrap iron or slag. The cooled melt is extracted with boiling water and the extract treated with lime, which causes the formation of the ferrocyanide and permits its crystallization, since it causticizes the soda present; the latter would otherwise crystallize with the ferrocyanide. The mother liquor is the so-called 'black soda' and contains sodium hydroxide, carbonate, cyanide, thiocyanate, and sulphide. This may be used instead of calcined soda in the original fusion and is said to give better results and render subsequent treatment with lime unnecessary.[209]

Phosphorus.

The sintering of pebble phosphate and of bauxite without impeding the combustion of the fuel is accomplished by using coke moistened with lime or alumina and subsequently mixed with the 'decomposing agent', soda ash, and sintered. $Ca(OH)_2$ forms in the pores of the coke and prevents penetration by dissolved salts etc., which impede combustion.[210] Thus 10kg. of pebble phosphate mixed with 6kg. of soda ash and 1·5kg. of coke are granulated and sintered in a blast roasting furnace.[211]

Crude calcium phosphate may be fused with aluminous material, e.g. bauxite, and a reducing agent such as anthracite in the presence of sulphur added as pyrites. Phosphorus vapour is produced with a readily fusible slag containing calcium aluminate and sulphide with aluminium sulphide. The slag is worked up to alumina by extraction with soda solution.[226]

Sulphides.

Sodium sulphide may be prepared commercially by an extension of the desulphurizing process for iron. Fusion of iron pyrites with sodium carbonate and half its weight of coal for 3hr. at 900°C. gives a product which may be extracted by water to form aqueous sodium sulphide. If the pyrites is heated in air with the carbonate sodium sulphate is obtained.[212]

Halogen Salts.

A continuous process for the preparation of sodium chlorate from sodium hydroxide and bicarbonate is described in a Russian paper. The mother liquor (from previous runs) is treated with 0·5g. of sodium hydroxide per ml. of solution and chlorinated at 95–100°C. with stirring. The temperature rises to 110–112°C. and when chlorination is complete the hot solution is filtered from the precipitated sodium chloride and cooled to 8–10°C. for 16–18hr., during which time the sodium chlorate crystallizes out. The product contains 96–97% of sodium chlorate and 1% of sodium chloride. The mother liquor is returned to the process. It can be treated with 1g. of sodium bi-

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carbonate in lieu of the hydroxide as described above; in this case there is no rise in temperature and no side reactions occur. The process avoids the usual evaporation.[213] Chlorine may be scrubbed from gases with aqueous soda containing 30–250 g./l. of sodium nitrite. Chlorine and oxides of nitrogen may be removed by a solution containing 30–60 g./l. of sodium nitrite and 40–190 g./l. of sodium carbonate at 30–85°C.[214] Aqueous sodium carbonate finds use as an antichlor.[215]

Sodium fluosilicate is generally prepared by utilizing the fluorine present in phosphorites. Hydrofluosilicic acid is liberated by sulphuric acid and reacts with sodium chloride to give sodium fluosilicate, Na_2SiF_6. The replacement of sodium chloride by carbonate is suggested, since it gives a product free from hydrochloric acid and diminishes operations in the factory.[216]

Oil and Gas Industry.

Refining Kerosene.

Caustic soda cannot be completely replaced by sodium carbonate since the reaction of the latter with naphthenic acids is reversible. At lower temperatures the retention of carbon dioxide in solution leads to a higher residual acidity, which is lowered by increasing the carbonate concentration. Complete purification can be effected by using carbonate equivalent to about 89% of the caustic usually employed and finishing with 11% NaOH.[217] Crude benzene or its homologues may be purified by bringing the vaporized hydrocarbons into contact with 1000 kg. of a granular mixture such as 70% of bog iron ore and 30% of soda ash, to which are added 1000 kg. of fuller's earth. The vapours of crude benzene passed through this at 100–150°C. gave (from 800 tons of crude) 789 tons of purified benzene suitable for motor fuel.[218]

Approximately 10 sec. is required for the complete removal of hydrogen sulphide with calcined sodium carbonate under conditions of turbulent flow. The carbonate can be regenerated simply by blowing away the hydrogen sulphide with air at 50–70°C.[219]

Sodium carbonate may be recovered from the spent 'doctor' solution (caustic soda) to the extent of some 240 lb. of Na_2CO_3 per 10,500 gall.[220] The reaction of hydrogen sulphide with sodium carbonate may be promoted by addition of 1–3% of a phenolic hydroxy oxidation promoter (such as the polyhydroxybenzenes) and 0·05 to 5% by weight of an oxidation promoter such as the sulphide ion. The solution after use contains the sulphur as sulphide and may be regenerated as above.[221] A 4% aqueous solution of sodium carbonate removes 90–95% of the hydrogen sulphide from a gas containing 2–15 g./cu. m. This is achieved by scrubbing in towers packed with Raschig rings. The regeneration is effected by heating to 50–55°C. under an absolute pressure of 110 mm. of mercury. Some of the carbonate is lost as thiosulphate and thiocyanate.[222] Soda ash is used in flooding oil wells in preferance to sulphide and cyanide solutions, both of which attack oil and the former the piping, while salt solution may drive oil from calcium carbonate formations.[223] The action of sodium carbonate as a flooding agent permits the recovery of oil by flotation, since it replaces the oil which wets the sand grains; the salt water is pushed ahead of the carbonate solution, preventing the deposition of insoluble compounds.[224]

It is interesting to note that high-efficiency heat exchange can be effected between descending molten sodium carbonate and cool rising hydrocarbon gas, the temperature of the latter mounting from 100 to 1700° F.[227]

The production of liquid carbon dioxide from flue gases can be achieved with savings in energy and coal by using an absorption train of sodium carbonate solution. The latter is pumped under 50 or 60 atm. pressure to a generator. The carbon dioxide is then liberated by heating at 270–280°C., when it passes (still under pressure) to a condenser where it is liquefied.[228]

A fluidized metallic catalyst (Fe_2O_3 70, Na_2CO_3 30%) of particle size 40–120 μ is used in the vapour phase purification of naphthalene by oxidising the impurities to carbon dioxide and water. The crude hot-pressed substance, which may contain approximately 2% of alkyl hydrocarbons, is vaporized and preheated with the calculated amount of air. It is then passed at 400°C. through the catalyst: 0·5 lb. per lb. of naphthalene per hr. is required, the naphthalene–air velocity being 0·1–0·5 ft./sec. at atmospheric pressure.[229]

Photography.

As a general rule potassium salts are replaceable by sodium salts in photography without any undue effect. The activities of hydroquinone developers containing in one case sodium carbonate and sulphite and in the other the corresponding potassium salts have been compared. At any given pH from 10·25 to 10·64 the potash developer was more active than the soda: in the absence of bromide fog developed more rapidly in the former, but with the addition of 2·5 g./l. of potassium bromide to the potassium reagent and 2·15 g./l. of sodium bromide to the soda developer, no difference in fog rate was noted.[230,231] Most fine grain and other developers contain large amounts of sodium carbonate.[232] The estimation of the sodium carbonate content in new or used developers is important.[233]

Utilisation of Surface Properties.

In the construction of canals, weirs, dams and other civil engineering projects, the porosity of a sandy soil can be decreased by running through it a water suspension of fine particles such as clay. The silting material may contain bentonite or a clay soil in which sodium carbonate is used as a dispersing agent. In some cases the water permeability of the sand may be decreased to 0·001 of its original value.[234] An inversion of this method is to flocculate (after impregnation) the highly stable thixotropic bentonite suspensions containing 3 to 5% of solid material by dilute solutions of aluminium chloride. This produces an impermeable layer some 5 cm. in thickness. An excess of sodium carbonate may neutralize the flocculating effect of aluminium chloride, but with regulated additions the time of flocculation may be controlled.[235] Peptization by sodium carbonate is used to provide drilling and casting muds often of a bentonite or sub-bentonite nature.[236-238] True soil stabilization can be achieved by forming a gel *in situ* with the aid of a mixture of sodium silicate and bicarbonate, which forms a silica gel holding grains of sand together in a stable semipermanent mass which can be excavated by an augur without sloughing or caving; concrete can be poured directly into the bore without the need of forms. A mixture of 12 parts by volume of N. sodium silicate, 60 parts of water and 28 parts of a solution of 6·6 lb. of sodium bicarbonate per 100 lb. of its aqueous solution gels in 45 to 60 min.[239]

Montmorillonitic raw material can be treated with sodium carbonate to obtain activated bentonites suitable for drilling muds. Thixotropic gels of high strength may be obtained in diluted aqueous suspensions with additions of sodium carbonate equivalent to the exchangeable bases in the soils.[240] The swelling abilities in water are increased three to five-fold. If the kaolinite ($Al_2O_3,2SiO_2,2H_2O$) content of a clay paste is considered and sodium carbonate deflocculant added to the extent of 5–10 milliequiv. of OH^- ions a slip of maximum fluidity is obtained.[277] On the whole a slip best satisfying the casting requirements demands a compromise between minimum rigidity and minimum apparent viscosity.[278]

In the manufacture of cement the wet grinding of materials can be accelerated by sodium carbonate in preference to silicate or hydroxide. The moisture content of the slurry can thereby be reduced.[241] It reduces the thixotropy of the slurry but does not improve the flow characteristics, since it

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does not affect the maximum shear curve.[242] The strength of pozzolanic material is increased at an early period by the addition of 0·1 to 0·5% of soda ash.[243] Subsequent presence of soda is injurious to Portland cement mortars, although relatively few natural waters contain enough to make them unsafe for use in concrete.[244]

As a preliminary step to the flotation of iron oxide ore 1 ton, together with 3kg. of soda ash, is ground with water to −65 mesh.[245] The presence of some soda is said to retard the disintegrating effect of other salts on Portland cement.[246]

Ceramics.

The use of sodium carbonate in the ceramics industry is largely confined to its alterant values. As a deflocculant it will alter the density, the viscosity, the thixotropic properties, and the pH of the slurry. It is often mixed with water glass (26°Bé.) for this purpose; the presence of gypsum is detrimental.[247] The latter has soil-flocculating properties. Fire-clays which have been deflocculated with sodium carbonate give better extrusion characteristics, and bricks have a greater dry strength, fired strength and absorption.[248] The effect of additions of sodium carbonate may be two-fold. Many of the lean clays have pH between 4 and 6; neutralization with sodium carbonate, raising their alkalinities, improves the extrusion quality for the manufacture of pressed ware and makes possible the manufacture of hollow or perforated ware from clays which would otherwise be unsuitable.[249] Various tannins (*quebracho* extract - a non-hydrolyzable sodium-tannin of polyphenolic type) promote the action of soda; together they can reduce the viscosity of a clay suspension by some 25%, widening the range of the viscosity minimum. Flocculation and thixotropy are eliminated, the optimum water content is lowered by about 20%, and the dry bending strength is increased.[250] Many failures in clays and slips can be attributed to some change in thixotropy, flocculation and peptization.[279]

The thermal expansion coefficient of various clays has been determined at 800–1000°C. 2–3% sodium carbonate additions increase this, together with the density when fired. This enables the clay to match the expansion coefficient of lead- and boron-free glazes.[251]

With plaster of Paris moulds, however, water glass is a more desirable thinning medium. There is no reaction with the calcium sulphate, but soda solutions form calcium carbonate crystals.[252]

Tanning.

A good deal of soda ash is used in this industry, in the preparation of antiseptic sprays for preliminary treatment of hides, in salting, where additions of carbonate provide a sodium-chloride brine of required pH[253](but may provoke putrefaction, if inadequate salt is used),[256] in unhairing by lime slurries to control the hydroxyl ion concentration and swelling;[254] and in degreasing.[255]

Chrome leather requires neutralization before further processing; the pH of the neutralized leather should be 5·0–5·2, the fresh cut of the chrome leather giving pH 4·6–4·8. Sodium carbonate by itself gives too high a pH, but mixtures with sodium bisulphite (45:55), with the addition of sodium phthalate (20–50%) are recommended.[257] The equilibrium and optimum conditions are complicated, some substances like the bicarbonates and borax producing low shrinking temperatures corresponding to easier co-ordination with chromium and forming complexes of lower tanning value.[258] The carbonate is said to be adsorbed by hide powder because the sodium hydroxide formed by hydrolysis is taken up.[259]

Water Treatment.

Soda can be used advantageously to reduce the acidity of soft water containing carbon dioxide. The process is specially useful for small works since only simple pH control is required. It permits the carbonate hardness to be increased to a greater degree than with calcium carbonate, and facilitates the formation of protective coatings. Total hardness is only slightly increased, and permanent hardness is decreased. The soda may be added before filtration or in some cases afterwards.[260] Where boiler-water may vary much in composition according to time and place, a general method involving some combination of lime treatment with sodium carbonate, bicarbonate, alum, zeolite, etc. may be necessary.[261] The lime–sodium carbonate treatment of feed water is generally recommended in Russia.[262] With certain waters the precipitation of sludges must be guarded against since some of them promote turbulent boiling.[280]

'Zeo-Karb H' is a hydrogen-ion zeolite which has been developed for the treatment of waters high in carbonates or bicarbonates; it removes all metallic ions present and replaces them with hydrogen ions by base exchange. The material can be regenerated with acid. The treatment removes all sodium carbonate and bicarbonate; a test sample initially contained $NaHCO_3$ 705, Na_2CO_3 42, NaCl 90 and Na_2SO_4 62 p.p.m. For some purposes it may be necessary to remove the mineral acids generated by by-passing some raw water.[263]

The decomposition of sodium carbonate in high-pressure steam boilers has been the subject of frequent investigation.[281] A graphical examination of available results has been made.[264]

The vapour pressure of carbon dioxide at 20°C. over a solution containing 1% of NaOH and 14·6% of Na_2CO_3 has been shown to be about 10^{-11} atm. In the paper in question an equation is given which relates the extent of dissociation to the concentration of sodium carbonate in the feed water, the total alkalinity in the boiler water, the steam pressure and other factors.[265] It is reported that the temperature and pressure in a boiler convert some 50 to 75% of the carbonate to hydroxide.[266]

The foaming of boiling solutions of 50:50 sodium hydroxide and sodium carbonate in the presence of sodium chloride and sulphate has led to a study of the hydrolysis of soda in the system as influenced by the variations in pressure in boilers.[267]

Conditions for the prevention of scale formation have been derived from the chemical equilibrium between calcium sulphate, magnesium carbonate, and calcium silicate on the one hand and sodium carbonate and phosphate on the other.[268]

The graphic treatment of the relations in the lime–soda–water system has been dealt with in a nomogram[282] and amplified in a later publication.[269]

The testing of water has received attention particularly in relation to the carbonate content.[50]

General Aspects of Use.

Sodium Carbonate.

Some attempt at classification of the large-scale uses of sodium carbonate has been made above. It should of course be emphasized once again that these form a supplement to Mellor's original Volume II. There are a number of minor processes in which no inconsiderable amounts of soda are used; disinfectants,[176] the paper industry,[270] weed killers,[271] micaceous insulating materials,[272] organic fine chemicals,[273] and the stabilization of latex from root rubber bearers.[295]

Patents have been granted in recent years for paint and varnish removers, often of complicated composition e.g. ammonia, soda, lime, glucose, alum, chalk and nitrobenzene in admixture with water,[283] but generally based on a lime/sodium carbonate formula avoiding undue use of caustic alkali.[275,276]

The storage of soda requires care, especially in the glass industry. Storage in sacks is equivalent to direct exposure to the atmosphere, while storage in large piles produces violent fluctuation from the mean moisture content; there may be 14·3% H_2O in the surface layers and 2·7% at 50 cm. below the surface.[274]

Sodium Bicarbonate.

In comparison with the carbonate, sodium bicarbonate is almost a fine chemical. Some of its uses are summarized here:- (i) as a conditioner or stabilizer: in agglomeration of powdered materials which may be treated with a solvent to soften the surfaces, moulded under pressure and partially fused to close the pores;[284,285] in lessening hygroscopicity in such mixtures;[286] for effervescent drink concentrates;[287] as a stabilizer of iodized salts (a dose of 0·2–0·5% by weight reduces the iodine loss during 3 months of storage in paper containers from anything up to 75% to only 16·84%);[288] and in maintaining or producing required pH values, for example 0·4% buffer mixture of 3:1 $NaHCO_3$:Na_2CO_3 will maintain the pH of sausage meat and increase the water-holding capacity of the finished sausage;[289] (ii) in the manufacture of sponge rubber when it is used as an auxiliary blowing agent to diazoaminobenzene,[290] and with amides $(CH_2N_2)_x$ such as melamine or cyanamide giving smaller and more uniform cells,[291] or biuret;[292] small quantities of gas are produced by mixing the bicarbonate with calcium chloride, the composition being placed at the top of some ball-point pens to give a pressure of about 1 atm. the evolution of gas stopping when the required pressure is produced.[293] (iii) in modifying surface conditions: 2% by weight of dry '*Drupex*' ($3Na_3PO_4$: $1NaHCO_3$) added to the pastes in working or grinding olives gives increased oils yields sometimes of improved quality.[294] Sodium bicarbonate for this purpose may also be coated as fine particles with 0·5 to 1% by weight of the stearates, palmitates or sebacates of calcium, magnesium, barium, aluminium, etc.[285]

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SODIUM CARBONATE AND BICARBONATE IN ORGANIC CHEMISTRY

There are some points in the behaviour of the carbonates towards organic reagents which should be mentioned. No attempt is made to deal with the many aspects of biochemistry or with the use of sodium carbonate in organic chemistry as a controlled source of hydroxyl ions.

Physical Properties.

A re-examination of extraction by the Soxhlet method shows that the solubility of inorganic materials in organic solvents has been neglected. The following values obtained[1] supplement the data in the section on Physical Properties:-

Solubility per 100 g. of Solvent

	Methyl alcohol	Ethyl alcohol 96%	Ethyl alcohol Dried with lime	Acetone, Ether Ethyl acetate
Na_2CO_3	0·3 g.	10 mg.	4 mg.	0
$NaHCO_3$	0·8 g.	15 mg.	15 mg.	0

The depression of the freezing point of water has been determined for some 217 aqueous solutions of sodium bicarbonate and for various Ringer solutions (xNaCl + yNaHCO$_3$).[2] The densities of a number of similar solutions were also measured.[3]

Equilibria in the ternary system sucrose–water–sodium carbonate at 30°C. have been further explored. A stable compound $C_{12}H_{22}O_{11},Na_2CO_3$ has been identified. The addition of sodium (or potassium) carbonate results in an initial decrease in the solubility of sucrose followed by a marked sudden increase with accompanying large viscosity increases in the aqueous phase.[4]

The solubility data for various kinds of celluloses indicate that the material dissolved by aqueous sodium carbonate is γ-cellulose. Rayon, practically insoluble, contains β-cellulose almost exclusively.[5]

Simple Reactions.

Crude calcium acetate dissolved in water at 80°C. and treated with soda yields some 78–80% of sodium acetate.[6]

The electrolysis of aqueous sodium acetate has been performed in the presence of various inorganic salts. The addition of 0·10 M. sodium carbonate prevents the formation of ethane; 0·25 M. potassium bicarbonate promotes the formation of methyl alcohol.[7]

The acid-base equilibria in $NaHCO_3$-H_2CO_3 systems is disturbed by salts of weak acids or weak bases because of hydrolysis. The physiological importance is that a salt of a feebly ionized acid renders alkaline any cell which adsorbs it, while the salt of a feebly ionized base confers acidity.[8]

The dissolution of salts in glacial acetic acid produces a number of double decomposition reactions. Sodium carbonate appeared to be the only salt noticeably solvolyzed by the acid with the liberation of carbon dioxide; calcium carbonate was not affected.[9]

Fatty acids when melted readily react with the decahydrate melted in its own water of crystallization. The compounds formed resemble the bicarbonate and are represented by the formula $Na_2H_2(CO_3)(C_nH_{n-1}O_2),xH_2O$. They can be used in place of soap and have a mild effect upon the skin. Organic nitrogen compounds exuded from the skin are insoluble in soap and caustic alkali but readily soluble in hot aqueous solutions of these salts.[10]

The highly diluted carbon monoxide in blast furnace gases may be converted into formate by pressure heating with 3·79 N. sodium carbonate solution at 220° and 60 atm. in an autoclave. Up to 90% of the calculated amount of formate is obtained, consuming 75% of the carbon monoxide in the gas.[11]

The heating curve of sodium formate shows its melting point to be 258°C. This is followed by decomposition to sodium carbonate, carbon monoxide and hydrogen at 308°C. and into sodium oxalate and hydrogen at 353–426°C. The change in the sodium carbonate can be expressed by $dx/dt = k(a-x)^2$ with k approaching the value for a bimolecular reaction. At 340°C. sodium oxalate begins to appear and the simultaneous parallel reactions are represented by $d(x+y)/dt = (k_1+k_2)(a-x-y)^2$, where k_1 is the velocity constant for sodium carbonate and k_2 that for sodium oxalate: k_1 and k_2 maintain a definite ratio. The relation holds for higher temperatures, confirming the parallelism and negating a possible chain reaction. If caustic soda is present the following reaction takes place:[12,13]

$$HCOONa + NaOH \rightarrow Na_2CO_3 + H_2.$$

In an experiment to determine whether it was possible to electrolyze aqueous salt solutions above the critical point it was shown that in the case of sodium carbonate and bicarbonate solutions at 400°C. the hydrogen evolved at the cathode reduces the carbon monoxide and carbon dioxide to formic acid.[14]

The catalytic decomposition of formaldehyde vapour by passage at 300–500°C. over sodium carbonate is very rapid. Considerable methyl alcohol is formed.[15]

When mercurous chloride is introduced with intestinal juice made strongly alkaline with sodium carbonate soluble and ionizing mercuric compounds are formed. The reaction also takes place with the bicarbonate, but not with sodium hydroxide; it is concluded that a readily dissociable complex containing $Hg^{++}Cl(CO_3Na)^-$ is formed.[16] Another suggestion is that colloidal mercury is formed with some 'soluble' mercuric oxide.[17]

Sodium bicarbonate is incompatible with alkaline bismuth ammonium citrate solution, since a white precipitate of basic bismuth carbonate is produced.[18]

When fermenting solutions are partially neutralized with carbonates the ratio of acetic to lactic acid changes. The carbonates remove one or the other of the acids: sodium carbonate neutralizes lactic acid more easily and therefore favours its increased production.[19]

Sodium and other alkali-metal carbonates heated with *α*-amino-carboxylic acids in aqueous solution give suitable intermediates for the manufacture of polymers. From Na_2CO_3 100 parts, glycine 75 parts, H_2O 500 parts, and methyl alcohol 1800 parts, added continuously over 1 hr., a white precipitate is obtained which on washing and drying gives 92 parts of a solid with the formula $NaO_2C.CH_2.NH.CO_2Na$. The process may also be used to purify α-amino-carboxylic acids by regenerating the acid from the above reaction product on boiling with barium hydroxide.[20]

Alkylcarbonic Acid Salts.

Passage of carbon dioxide into the appropriate alkoxide solution gives salts of the formula $NaOCO_2.C_nH_{2n+1}$. From sodium methoxide is obtained MeO.COONa, which decomposes at 310°C. to give CO_2 84·5%, C_2H_4 3·7%, CO 11·8%, some formaldehyde, and Na_2CO_3 43·4%. The thermal capacity is 0·2974, the density 1·955 g./c.c. and heat of combustion 146 kg.-cal. per mole. Similar data are available up to and including the butyl compound.[21]

The aralkyl carbonates are described in a patent specification as useful additives to synthetic resins. The aralkyl chloride (e.g. benzyl, etc. or complicated mixtures from chloromethylated aromatic substances) is heated for 8-24 hr. at 90–120°C. with sodium carbonate or bicarbonate in the presence of a catalyst chosen from the tertiary amines. The preferred mole ratio of sodium carbonate to the aralkyl halide is 1·5:1. The action of sodium carbonate is specific: other alkali or alkaline earth carbonates will not do.[22]

Granular Raney-type catalysts (e.g., Al 40–50:Cu 50–60:Zn 0–5%) effect dehydrogenation of *cyclo*hexanol to *cyclo*hexanone. There is a secondary activity of dehydration; this, however, may be strongly inhibited by adding to the catalyst moderate quantities of sodium carbonate or other alkalis obtained by immersion in solutions of up to 10% concentration. The dehydrogenation activity is not affected.[23,24]

Much work has been done on the important problem of the sterilization of sodium bicarbonate solutions. The most successful methods appear to be the following: (i) sterile aqueous sodium carbonate is treated with excess of sterile gaseous carbon dioxide under strictly sterile conditions;[25,26] (ii) sterilization in streaming steam at 100°C. for half-an-hour is rapid and reliable and causes less loss in bicarbonate (0·0924 g./l.) than more prolonged treatments which may result in as much as 0·2518 g./l.;[27] (iii) the solution may be autoclaved in hermetically sealed containers provided they are not more than 0·9 full, the extent of decomposition of HCO_3^- to CO_3^{--} being negligible.[28]

Sodium carbonate has some small germicidal activity, and increases markedly similar activity in caustic soda and in soap solutions.[29] At the same hydroxyl ion concentration it is more efficient than caustic soda.[30] In small concentrations in solution (20,000 p.p.m.) it is decidedly harmful to rats and other small animals and reproduction is interfered with.[31] The toxicity to plants has been referred to in the section on Occurrence; it is twice as toxic as the bicarbonate. The infertility of black alkali soils is due generally to sodium chloride and sulphate. Small concentrations of the carbonate appear to act as stimulants to plant growth.[32,33]

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SECTION XXXVII

SODIUM NITRATE

By D. A. PANTONY

Occurrence

Whilst by far the greatest deposits of naturally occurring sodium nitrate are to be found in Chile (estimated reserves in 1942 were 168×10^6 long tons),[1] other sources of an interesting but minor nature have been reported. Analyses of calcareous rock found at Gibeon, South West Africa, have shown that the deposit contains several soluble sodium salts, including up to 16% of sodium nitrate, together with smaller proportions of sodium and potassium chlorides and sodium sulphate, but no iodine and little or no phosphate.[2] Sodium nitrate in concentrations up to 7% was being exploited in the Qena district of Egypt to the extent of 113,000 tons per annum in 1940. A thorough examination of the south-western and western states of the U.S.A. has shown that sodium nitrate is very widely distributed and is occasionally to be found in an almost pure form; the most promising of the localities is at Amargosa, California, where uneven deposits occur averaging 2·5% of sodium nitrate in 6in. layers.[3,4] In the San Luis Potosi and Queretaro districts of Mexico[5] there are pockets of potassium nitrate which frequently contains high proportions of sodium nitrate, and minor deposits, possibly worked locally, have been reported in Bolivia and Peru. Efflorescences of sodium and potassium nitrates on outcrops in the Sahara Desert have been examined.[6] Uniform deposits of potassium nitrate with carbonate and sodium nitrate are said to occur in the Lake Lahontan region of Oregon, but no analytical figures for sodium have been given.[7] Mention has been made of the mixed nitrates, sulphates and chlorides of sodium, potassium, magnesium and ammonium occurring in Turkestan[8] and of the 'saltpeter' that can contain up to 41% of sodium nitrate at Tschetscha in the Caucasus.[9] Local extraction and possible large-scale recovery in times of emergency have been suggested,[5,6] but forecasts are not optimistic. However, an historical account of the extraction and conversion to potassium nitrate of sodium nitrate in Kentucky during the War of Independence has been given.[10] Mineral waters of Ericeria, near Lisbon, contain appreciable quantities of sodium and of nitrate[11] and, similarly, waters in the sub-soil of Rome contain the salt but are free from nitrite and ammonium salts.[12] It has been stated that water percolating through the tuff ejected by Cordilleran volcanoes contains up to 67 p.p.m. of sodium nitrate.[13]

The Origin of Sodium Nitrate Deposits

There is still no agreement on the mode of genesis of world sodium nitrate deposits and the various theories have been reviewed from time to time.[14-19] Briefly, the theories may be classified[20] as the 'inorganic', invoking volcanic or atmospheric origins, and the 'organic' theories, envisaging microbiological processes to produce the nitrogen compounds that finally appear as nitrates. Most theories are inadequate mainly because they seize on one aspect of the chemistry or morphology of the deposits or generalise from the study of a single sodium nitrate deposit, without sufficient regard for the data for other localities. Probably the mode of genesis of the various deposits may differ slightly among the several localities, but one feature they all have in common: the areas are arid and the deposits are to be found in or just beneath approximately bowl-shaped surfaces.

Among the inorganic theories may be mentioned: (*a*) the air oxidation of ammonium compounds ejected from volcanoes, probably with biochemical assistance[11,21,22] or by means of an inorganic catalyst such as volcanic dust (pozzolana)[12,23] or by other means;[13,24] (*b*) action of electrical discharges on the nitrogen and oxygen of the air with formation of ozone and then nitric acid[25] which is then able to act on sodium salts derived either from guano or local sodium-bearing rocks[17,26] or on air-borne sodium chloride from volcanoes[27] or the sea.[28] In this connection it has been suggested that ozone also reacts with hydrogen chloride derived from the sea with the formation of chlorine heptoxide which indirectly provides potassium chlorate and sodium iodate from the native soil minerals,[28] and, as a variant, that acid vapours from marine decomposition and sea-water evaporation and volcanic origins act on native sodium-bearing rocks on the seaward side of the Chilean pampa.[29] An attempt has been made to relate the genesis of sodium nitrate deposits with the oxidation–reduction potentials of ions known to be present in and near the deposit.[30]

The organic theories generally require decomposition of marine growths and subsequent action of the nitrate deposits with sodium chloride.[31–33] Against the inorganic theories is usually cited the remarkable number of minor and trace elements, especially iodine, to be found in the natural sodium nitrate deposits or *caliche*. Such an abundance serves as a strong argument for the use of Chile saltpetre as a fertiliser,[34–38] and it is notable that the proportions of some of these impurities are of the same order as those found in living organisms. Typical run-of-mine *caliche* may yield the figures in Table I:

TABLE I. - ANALYTICAL DATA FOR CHILEAN *CALICHE*

	I[36]	II[36]	III[39]
Sodium nitrate	35·0%	21·5%	8 to 25%
Potassium nitrate	1·0	1·0	2 to 3
Sodium chloride	32·0	40·0	8 to 25
Sodium sulphate	8·0	2·0	2 to 12
Magnesium sulphate	1·0	tr.	0 to 6
Calcium sulphate	5·0	4·5	2 to 6
Sodium iodate	0·15	0·08	0·05 to 0·1
Insoluble	16·05	29·92	–
Moisture	1·8	1·0	–
Sodium borate	–	–	1 to 3
Potassium perchlorate	–	–	0·1 to 0·5

For exported Chilean saltpetre the analyses in Table II have been given.[36]etc.

Spectrographic traces of titanium, vanadium and gallium have also been reported.[40]

The analytical data have been used to support the biological theories,[34,41] although it has been pointed out that iodine, in particular, occurs in similar proportions in many rocks as well as in animal and vegetable products.[42] Emphasis has been laid, however, on the disparity in magnitude between deposition reasonably attributable to continuous microbiological fixation or to precipitation of nitrogen compounds from the air or from volcanic emissions

TABLE II. - ANALYTICAL DATA FOR CHILE SODIUM NITRATE

	Soluble	Insoluble
Potassium (as K_2O)	1·5%	-
Magnesium (as MgO)	0·1%	-
Chlorine	0·4%	-
Iodine	0·04%	-
Boron	0·04%	-
Manganese	0·002 mg.	0·06 mg./100 g.
Zinc	0·05 mg.	0·6 mg./100 g.
Chromium	0·001 mg.	0·001 mg./100 g.
Iron	0·05 mg.	1·0 mg./100 g.
Aluminium	0·001 mg.	0·005 mg./100 g.
Nickel	0·001 mg.	tr. /100 g.
Lead	0·05 mg.	0·2 mg./100 g.
Silver	0·001 mg.	0·002 mg./100 g.
Tin	tr.	-
Molybdenum	0·003 mg.	- /100 g.
Copper	0·07 mg.	- /100 g.
Strontium	0·06 mg.	- /100 g.

and the great size of the Chile deposits, and on the lack of phosphate in the deposits, indicating that guano is unlikely to be a primary source. The enormous reserves of combined nitrogen found in certain ocean localities suggest that the Chile *caliche* may have originated from botanical accumulations in a sea or large lake which, owing perhaps to isostasy to the geological fault represented by the Andes, or to general recession of the seas, slowly became isolated and ultimately dried up completely in the arid climate of the area. Possibly, small contributions may have been made continuously since that time by other means discussed above. The process of daily evaporation and nightly cooling, combined with the different solubilities of sodium phosphates and sodium nitrate, is claimed to be sufficient to explain the relative absence of phosphate, the presence of sodium chloride pockets and, together with normal geological processes, the formation of the *costra* or overburden.

Production of Sodium Nitrate

(a) *From Chilean Caliche.*

A very large number[19,20,43-69] of reviews, histories, statements of problems and comparisons with nitrogen fixation industries, of which the references cited are an example, has appeared over the past forty years. Of particular interest are discussions in the period shortly after 1918, when the relatively rich (>16%) sodium nitrate-bearing ore had been worked out, interference from sodium sulphate was becoming serious, competition from the nitrogen fixation industries was seriously felt, and the caliche industry was suffering from economic pressure from the Chilean government. Many of the fears expressed at that time either proved groundless or have been nullified by strong economic measures or by more liberal taxation, so that the output of Chile saltpetre, with minor fluctuations, has become remarkably steady over the past few years. Production figures given in Table III[19,39,66,70] are selected to show the response of output to world conditions, and the comparison with world synthetic nitrogen compounds, data for which are given in column 2 of Table 3, calculated as tons of sodium nitrate.

The principles of the method of extraction have not changed since the early days of *caliche* mining: the ore is broken up with explosives and the soluble salts are extracted with warm or hot water. In the Shanks process,

TABLE III. - WORLD PRODUCTION OF NITROGEN COMPOUNDS

Nitrate Year	Production Figures (World) as $NaNO_3$ (metric tons)	
	Synthetic Nitrogen	Chile Saltpetre
1901/1902	660,000	1,272,000
1906/1907	1,086,000	1,747,000
1911/1912	1,704,000	2,437,000
1916/1917	3,179,000	2,715,000
1921/1922	3,698,000	1,591,000
1926/1927	7,040,000	1,812,000
1931/1932	9,143,000	806,000
1936/1937	15,845,000	1,562,000
1941/1942	-	1,371,000
1946/1947	16,046,000	1,526,000
1951/1952	32,128,000	1,446,000
1955/1956	-	1,462,000

which is still worked today on high-grade ($\nless 13\%$ sodium nitrate) ores, the *caliche* and *costra* are blasted together and, after size reduction to 8 inch pieces, the high grade material is hand-picked and further crushed to 2·5 inch mesh. The sodium nitrate is leached in boiling water for 12 to 15 hours in vats of 50 to 90 tons capacity. After the slimes have settled, the solution is allowed to crystallize at atmospheric temperature and the crystals of sodium nitrate are separated and dried.[39,63] Various improvements[71] such as accelerated evaporation of liquors,[72-75] beneficiation of the ore,[76] liquid ammonia extraction and separation[68] and other procedures[63,77-82] have been suggested but, in general, have not been successfully applied. The main problems of settling of the slimes[73,75] from a hot process and corrosion[83,84] remained. The more versatile method, worked in the Guggenheim process,[39,85-92] involves extraction in warm solution (35° to 50°) after fine-crushing of the ore. The extraction is carried out in tanks of 7,500 to 12,000 tons capacity and, after removal of insoluble material, the solutions are cooled artificially to 7° to 10° in order to crystallize out the sodium nitrate. Some attempts to evaporate the mother liquors for further recovery have been unsuccessful,[75,80,93,94] but recent procedures to recover other salts, such as potassium nitrate, sodium sulphate, magnesium salts and boric acid, as well as some sodium nitrate, by evaporation[39,95] have proved economic. Similar, but less exhaustive, examination has been made of the salt pans of South Africa, where sodium nitrate could be recovered after separating sodium carbonate, magnesium and calcium salts, etc.[96]

The problem of separating sodium nitrate from other soluble salts in *caliche* has been the subject of much investigation. Solubility relationships have been discussed;[97] the problem of formation of darapskite, $NaNO_3,Na_2SO_4,H_2O$,[98] a fairly stable double salt, led to some trouble in the Shanks' process[81] but more so the Guggenheim process.[99] The chemistry of this double salt in is discussed below. Empirically, its formation had been prevented by addition of 'weeping' *caliche*[100] (*i.e.*, or containing glauberite) ore stabilizers' such as potassium, calcium or magnesium salts,[87] especially the sulphates.[88] Phase-equilibria studies show that the double salts such as astrakanite, $Na_2SO_4,MgSO_4,4H_2O$, ('protective compounds') are preferentially formed and, in addition, the settling of the slimes is accelerated.[68] The problem of borax, the presence of which is penalized in the sale of Chile saltpetre as a fertilizer, has been investigated.[101] Borax is largely eliminated by careful crystallization, but it can also be removed by precipitation as boric acid or calcium borate.

Sodium nitrate tends to deliquesce on storage; this undesirable property has been overcome by granulating the salt by heating it to 340° and spraying the melt through fine nozzles before solidification,[39,102,103] when some further purification also takes place.[104] More recently, the 'Krystal process' – a dynamic crystallization method – has been introduced,[39] and an alternative granulating operation in which the water is flash-evaporated from superheated concentrated solutions has been suggested.[105,106] Various other 'stabilizing' procedures have been proposed from time to time: patents refer to mixing, or formation of mixed crystals, with minor proportions of calcium carbonate,[107,108] other nitrates[109,110] (especially ammonium nitrate[111] the use of which has been studied systematically[112]) ferrous or magnesium hydroxide,[113] pumice or other solids,[114,115] fluidizing agents such as metal stearates, etc.,[116] or to coating the crystals of sodium nitrate with various inert materials which may, for example, decompose in the soil.[117]

(b) *Other Methods of Production.*

Only a relatively small part of the world's nitrogen fixation industry is concerned with the production of sodium nitrate, but some is indeed manufactured in America, in Germany and probably in Russia. Nitrogen oxides, produced by oxidizing ammonia or by direct combination of nitrogen and oxygen, are absorbed in a solution of sodium hydroxide or carbonate[118] or, it has been suggested, sulphide.[119] The simultaneous formation of nitrite and nitrate and the subsequent oxidation of the former, most efficiently carried out under pressure in the presence of air and nitric acid, has been intensively studied.[120-124] The possibility of preparing sodium nitrate by the action of nitric acid upon sodium chloride (possibly derived from sea-water) has been examined and reviewed[125-127] and several patents have been taken out on the method.[128-132] The reaction can be carried out at higher temperature[133,134] or with the aid of a base-exchange medium.[135] The value of the by-product chlorine from some of these processes makes the method attractive.

The use of a double-decomposition reaction between sodium chloride, carbonate or fluoride and ammonium nitrate,[136-144] barium nitrate,[145] lead nitrate[146] or calcium nitrate has been discussed, as also has the use in this connexion of liquid ammonia as solvent[147-151] and of a base-exchange material such as a zeolite.[152-158] The simultaneous production of potassium and sodium nitrates from sylvanite has been thoroughly investigated and details of manufacture suggested: treatment of an aqueous solution with ammonium nitrate at 20° is recommended.[159] An alternative method involves increasing the potassium:sodium ratio of sylvanite to that of glaserite by adding potassium chloride, whereafter addition of ammonium chloride and sulphate and ammonia precipitates glaserite; this is then treated with calcium carbonate and nitric acid to form sodium and potassium nitrates.[160,161] Leucite can also be used as a starting material.[162] An apparatus whereby sodium and potassium nitrates can be separated by a procedure involving recycling of the mother liquors has been described.[163]

The action of nitrous fumes on waste sodium nitrite,[164] or calcium carbonate–sodium hydroxide[165] liquors, or the absorption of the fumes in a ferric oxide–sodium nitrate mixture that has been heated to 700° to 900°,[166] have been suggested as minor methods of production. The preparation of chlorine dioxide by treating sodium chlorate with nitrous fumes yields sodium nitrate as a by-product;[167] nitrous fumes can be absorbed in sodium hydroxide derived as a by-product from other processes.[168]

Sodium nitrate frequently appears as a by-product in the treatment of phosphates and phosphate rocks with nitric acid or nitrogen oxides in the presence of sodium salts.[169-175] Sodium formate,[176,177] derived from sodium sulphate, lime and carbon monoxide, or sodium oxalate,[178] when neutralized in

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the cold with dilute nitric acid, yields the free organic acids and sodium nitrate. Sodium bicarbonate obtained in the ammonia-soda process can be treated either with carbon and nitrogen to give sodium cyanide which is subsequently oxidized by air,[168,175,179-181] or with ammonium nitrate[182] or nitric acid,[183] to give sodium nitrate. Treatment of sodium sulphate with nitric acid in the presence of the correct proportions of calcium carbonate,[184,185] or with calcium nitrate,[186,187] the reactions being catalyzed with manganous salts,[188] has been suggested as a preparative method, as has the action of nitric acid on a mixture of sodium fluoride and silica, yielding sodium silicofluoride as the main product.[189]

(c) *Laboratory Methods of Preparation.*

The formation of sodium nitrate by the action of sodium peroxide on liquid or gaseous dinitrogen tetroxide below 140° has been described; above 140° the reaction, which is then more rapid, yields both the nitrite and nitrate, but after prolonged contact of the reagents, especially at higher temperatures, the latter predominates.[190] In liquid ammonia, sodium displaces ammonium from its nitrate forming sodium nitrate together with sodium nitrite, hyponitrite and amide.[191] Minute amounts of sodium nitrate, discovered on the surface of rock salt, arise from the action of the α-rays of polonium on nitrogen dioxide from the air in the presence of moisture.[192] It has been reported that regularly oriented microcrystals of sodium nitrate may appear upon sodium chloride crystals when these are in the presence of nitric acid or evaporating solutions of barium, lead or silver nitrate solutions or, to a smaller degree, nitrogen dioxide vapour.[193]

Large single crystals of sodium nitrate, intended for optical purposes, have been prepared by controlled slow cooling of the molten salt;[194-201] they have also been deposited on calcite, dolomite, etc.[202]

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Uses of Sodium Nitrate

Some of the reversible processes discussed briefly above have been proposed as methods of preparing other nitrates: thus potassium nitrate can be obtained by the action of crude potassium chloride on sodium nitrate solution in the presence of a peroxide or air to render iron insoluble,[203] and ammonium nitrate can be prepared by the analogous reaction of ammonium chloride on sodium nitrate.[204] Separation of the products may be achieved by sifting the crystals or by fractional crystallization,[205] although equilibrium studies indicate that the maximum yield to be expected is only 9·7% at 0° and 21% at -10°.[206] Ammonium sulphate is suggested as a more suitable starting material, since the co-product sodium sulphate can be removed by precipitation with ethanol. Sodium nitrate can be partially substituted for sodium chloride in the initial stages of the Solvay process,[207] and reaction with sodium nitrate has been proposed as a method of recovering potassium, as nitrate, from the waste gases of cement kilns.[208]

Caliche itself has long been regarded as a potential source of potassium nitrate,[39,209] and the preparation of this salt from *caliche* by reaction with potassium chloride has been discussed.[210] Extraction of sodium chloride, mixed with a little sodium sulphate, from mother liquors from the Guggenheim process, after removing elementary iodine by absorption in carbon, has been proposed,[211] and alumina and nitrogen oxides may be prepared by the action of heat on a mixture of *caliche* and aluminium sulphate.[211] Similarly, the action of acidic substances, for example, acidic silicates, when heated with *caliche* may produce nitrogen oxides for nitric acid production,[212] and several other possibilities for minor uses of sodium nitrate have been discussed.[213]

Very many publications have appeared on the application of sodium nitrate as a soil additive and nitrogenous fertilizer. In assessing the value of comparisons with other nitrogenous fertilizers, care must be exercised owing to the large number of very active trace substances[214,215] that are to be found in Chile saltpetre, since these may have an outstanding, and unexpected, beneficial effect on some plants in certain localities. The effects of sodium nitrate on soil permeability to water, on nitrogen availability to plants, on the pH of treated soil, and on ion-exchange properties of the soil and soil nitrification have been studied extensively.[214,216–238] In general, soil microstructure is slightly affected adversely by deflocculation on continuous heavy dosage with sodium nitrate; pH rises with continued use on acid soils and potassium assimilation by plants[239] is reduced except where the sodium ions accumulated at a considerable depth, and the availability of nitrogen to plants and, for example, to biological systems in compost,[240] is high. When refined Chile saltpetre is employed, the trace elements present have an additional beneficial effect in certain circumstances.[241,242] Individual experiments on sugar beet or cane,[227,243–248] on potatoes,[249,250] on cereals and grass,[237,251–262] on fruit trees[233,263,264] and in association with ground phosphate rock,[265] show that additions of sodium nitrate or, better, Chile saltpetre or sodium nitrate mixed with a little borax, produce desirable results comparing favorably with those of other nitrogenous fertilizers except where the calcium content of trees is markedly reduced after long usage. Today, most of the output of natural sodium nitrate finds special use in agriculture as a boosting fertilizer in certain parts of the world, especially on crops that metabolise both nitrogen and sodium.[265] The role of nitrate in its reduction in living plant cells has been studied, but it is difficult to establish a mechanism.[267] Ferrous ions, which when present in soils are toxic to plants, have been oxidized successfully with sodium nitrate in field trials.[268,269]

Inhibition of alkaline corrosion ('caustic cracking') of ferrous and some non-ferrous materials is successfully achieved with dilute solutions of sodium nitrate,[270-278] but sodium nitrate can cause intercrystalline cracking of internally stressed mild steel.[279,280] Conflicting reports have been given on the inhibition of corrosion in chloride solutions[281,282] by sodium nitrate. The mechanism of the anti-corrosion effects involves the retardation of anode processes of corrosion,[283] for example, by the enhanced passivity of the ferrous surfaces.[284] The use of sodium nitrate as a nitriding agent[285] and as a constituent of phosphatizing solutions[286-288] for the protection of iron and steel has been recommended. Elimination of carbon, silicon and, especially, sulphur during the open-hearth process for steel-making is accelerated by additions of sodium nitrate with ferrosilicon to the slag[289-292] and the properties of cast iron are improved similarly.[293-296] Stainless (high-chromium) steels can be cleaned and descaled advantageously with fused mixtures which contain some sodium nitrate,[297-301] and a solution containing sodium nitrate and other salts has been recommended as a basis of treatment prior to microscopical examination of steels[302] and aluminium.[303] Sodium nitrate has also been used successfully to maintain the cleaned aluminium surface necessary in the nickel-plating of aluminium objects[304] and as a constituent of an oxidizing melt used to deposit an insulating film on nickel-chromium[305] and nickel-copper[306] wires and other alloys.[307]

Sodium nitrate still finds application in the manufacture of explosives,[308-310] explosive jellies,[311] smokeless powders,[312] special explosive mixtures[313] and solid-fuel propellants.[314] The use of the salt in 'sweetening' sewage and industrial effluents has been very successful, mainly owing to its ability to oxidize hydrogen sulphide[315] and organic matter[316-318] even in great dilutions, and the possible use of sodium nitrate as a larvicide, bactericide and enzyme inhibitor has been examined.[319] Sodium nitrate has been reported as being toxic to animal[320,321] and microbiological life[322-325] so that it has been applied in the pickling of meat,[322] and the difficulties encountered in such use owing to reduction to nitrite have been discussed.[326,327] On the other hand, sodium nitrate has been used as a constituent of culture media.[328]

The use of sodium nitrate crystals for optical purposes, where their birefringence is equal to that of calcite, has been suggested,[329,330] and its addition, in small proportions, to glasses in order to form 'colourless iron' from ferrous ions that may be present has been investigated and recommended.[331-333] Mixtures of fused salts containing sodium nitrate have been recommended for use as a heat-transfer medium,[334-337] and a 1:1 mixture of sodium nitrate and nitrite is suitable as a salt bath over the temperature range 200° to 500°.[338,339] The salt has also been used as a constituent of screening smoke.[340]

The use of sodium nitrate to produce nitrogen oxides in the lead-chamber process for the manufacture of sulphuric acid has been thoroughly examined by several workers:[341-344] its cheapness, relative to nitric acid, may outweigh the disadvantages of undesirable sodium bisulphate formation. Solutions of the salt can be used in the flotation concentration of chalcopyrite ores, when the slimes become less unmanageable and the subsequent breaking down of the froth is more readily achieved.[345] Electrical carbon brushes containing sodium nitrate can function satisfactorily at -60° and in an oxygen-free atmosphere.[346] While the presence of sodium nitrate decreases the strength of cement,[347] an oil-sand cement containing the salt has been prepared.[348] Sodium nitrate has also found application as a gelatinization inhibitor for starch-glues,[349] as a constituent of a solution for rendering paper suitable for wet electrolytic recording[350] and in a recipe for flexibly coating electric cables.[351] The effects of sodium nitrate on the formation of cellular rubber[352] and on the absorption of sodium hydroxide by cellulose[353] have been investigated.

In the chemical and mineral industries, sodium nitrate finds a possible application in the manufacture of potassium nitrate from a wyomingite pegmatite

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which is pressure-leached at 200° and 200 lb./sq.in. with concentrated aqueous sodium nitrate.[354] Natural anhydrite can be hydrated by use of an aqueous solution containing, *inter alia*, sodium nitrate[355] and the salt can be used as a lixiviating agent in the treatment of spodumene in the extraction of lithium as its halides.[356] Calcium chromate can be prepared in a process similar to the ammonia-soda process by replacing sodium chloride by sodium nitrate and adding sodium chromate.[357] Sodium cyanate is purified from entrained cyanide by fusing with sodium nitrate.[358]

In the laboratory, the melting point of sodium nitrate has been used as a reference standard in thermal analysis,[359] and the ice–sodium nitrate eutectic (f.p. -18•5°) has proved satisfactory as a cryoscopic transition point.[360] An investigation has been made into the behaviour of a fused-salt mixture containing lithium (30 mole %), sodium (17 mole %) and potassium (53 mole %) nitrates and potassium chloride (0•5 mole %) as a polarographic medium: reductions of several bivalent ions proceed reversibly and their half-wave potentials are quoted.[361,362] In several physicochemical investigations sodium nitrate has frequently been used as a typical 1:1 electrolyte and to provide a constant or regulated ionic strength of an inert electrolyte. Examples of such uses are to be found in the following investigations: rate of decomposition of hypochlorous acid,[363] rate of hydrolysis of allyl halides,[364] of methyl propionate,[365,366] and of ethyl formate;[367] the solubilities of silver propionate and butyrate,[368] arsenious oxide,[369] nickelous hydroxide,[370] lead sulphate,[371] cadmium and manganese oxalates[372] and silver chloride[373] under various conditions; the behaviour of the uranyl ion to electrophoresis[374] and solvent extraction;[375] the salting-out of benzoic and phenylacetic acids,[376] ethyl acetate[377] and various other organic substances;[378] the study of the acidity function of solutions[379] and the ionization of acetic acid;[380,381] studies in the primary salt effects of colloidal electrolyte solutions,[382] the coagulation of aerosols,[383] of ethylhydroxyethylcellulose solutions[384] and the precipitation of silver thiocyanate and iodide;[385] the behaviour of surface-active agents under various conditions;[386,387] the mechanism of ion-exchange substances;[388,389] the cryoscopy of the sodium sulphate decahydrate–sodium sulphate transition point,[390] the freezing of supercooled water[391] and the vapour pressure lowering of ethanol–water systems.[392]

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Physical Properties of Sodium Nitrate

Solid Sodium Nitrate.

The similarity of sodium nitrate crystals to the trigonal calcite system has been recorded by several workers,[1,2] but sodium nitrate and calcite are not isomorphous and the mechanism of growth of sodium nitrate on the crystals of calcite is similar to epitaxy.[3] *X*-Ray investigations show that the crystal lattice is rhombohedral with sides of $6{\cdot}3108 \times 10^{-8}$ cm. with an angle of 47° 15′ 59″ between them.[4] The co-ordinates of the atoms (if the sides of the rhombohedron are taken as unity and the sodium ion is assumed to be at (0,0,0)) are:[2] sodium at (0,0,0) and (1/2,1/2,1/2); nitrogen at (1/4,1/4,1/4) and (3/4,3/4,3/4); oxygen at $(\beta,1-\beta,0)$, $(0,\beta,1-\beta)$, $(1-\beta,0,\beta)$, $(1/2-\beta,\beta-1/2,1/2)$, $(\beta-1/2,1/2,1/2-\beta)$ and $(1/2,1/2-\beta,\beta-1/2)$ where β is very nearly 1/4. A theoretical treatment[5,6] gives conflicting results which may be explained by unaccounted energy of the oxygen ions. The nitrogen-oxygen distance is given as 1·20 A.[7] 1·22 A. and 1·09 A.[9] The divergence from theoretical values is attributed to electrostatic effects which lead to smaller distances. The nitrate ions have been shown to lie in a plane normal to the trigonal axis of solid sodium nitrate and the absorption of light observed at 3000 A. in solution manifests itself only in this plane in the solid state.[10] The sodium ions form a triangular network in the basal plane of the crystal with sides of 5·06 A.[11] The structure has been used to explain the epitaxy of anthraquinone crystals grown on sodium nitrate crystals, where orientation occurs parallel to the bisectors of the rhombohedral obtuse angle.[12] The epitaxy of several organic crystals sublimed on to sodium nitrate has been examined;[13] for example, *o*-aminophenol attaches itself *via* its (100) axis,[14] dimethylglyoxime orients about its *b* axis with elongation along the b_0(010) axis.[15] The crystallization of thin gold films on the salt has also been studied.[16] It has been pointed out[17] that thin (10 A.) films of many salts may show orientation dependent on the crystal substrate, but at a thickness of 150 A. random orientation occurs, and that the orientation of deposits from vapour and from solution are not necessarily identical.

A gradual but reproducible transition of an endothermic[18,19] nature occurs in the structure of sodium nitrate beginning at approximately 150° and ending at 275°: other shorter ranges listed may be due to insensitivity of the method of detection or to errors in calibration of thermometric apparatus. The transition has been investigated by means of solubility, thermal capacity, optical, thermal expansion, specific heat, differential thermal analysis, electrical conductivity and *X*-ray diffraction measurements.[19–29] The transformation has been shown not to be a macro polymorphic transition since mica can be used for seeding molten sodium nitrate to produce ordered but small crystals of the salt: this is not typical of materials undergoing gross transitions between the melting point and room temperature. Similar seeding results are obtained from a saturated aqueous solution.[11] The transition is believed to be due to a restricted internal rotation of the nitrate ions in the crystal, probably about an axis through a nitrogen atom and perpendicular to the plane of the group – *i.e.*, round a trigonal axis of the crystal. The rhombohedral lattice has sides of 6·32 A. and 6·56 A. with an angle α of 47° 14′ and 45° 35′ at 25 and 280° respectively.[21]

The plastic deformation and development of slipping zones of sodium nitrate under load has been studied.[30–32] The density of the salt has been redetermined as 2·261 at 20°[33] and (d_4^0) 2·26536 ± 0·00017[34] and the values at lower temperatures are given in Table I, together with those of the molecular volume.[35]

TABLE I. - DENSITY OF SODIUM NITRATE

Temperature (°C.)	*d* (g./c.c.)	Molecular volume
23	2·263	37·56
17	2·261	37·60
−78	2·285	37·20
−183	2·308	36·83
−194	2·310	36·80
−273	2·32 (calc.)	36·7 (calc.)

The elastic constants (× 10^{11} dynes/sq.cm.) are:[36] C_{11} 8·67, C_{33} 3·74, C_{44} 2·13, C_{12} 1·63, C_{13} 1·60 and C_{14} 0·82. The compressibility of sodium nitrate shows variation with crystal orientation, the much greater coefficients of pressure (in the expression below) parallel to the trigonal axis showing an abnormal temperature coefficient.[37] Where p is the pressure in kg./sq.cm.:-

$$-\Delta l/l_0 \text{ (perpendicular to axis)} = 7{\cdot}093 \times 10^{-7}p - 5{\cdot}88 \times 10^{-12}p^2 \text{ at } 30^\circ$$
$$\text{and} = 7{\cdot}643 \times 10^{-7}p - 4{\cdot}41 \times 10^{-12}p^2 \text{ at } 75^\circ$$

$$-\Delta l/l_0 \text{ (parallel to axis)} = 24{\cdot}36 \times 10^{-7}p - 23{\cdot}5 \times 10^{-12}p^2 \text{ at } 30^\circ$$
$$\text{and} = 23{\cdot}36 \times 10^{-7}p - 21{\cdot}4 \times 10^{-12}p^2 \text{ at } 75^\circ$$

Whence

$$-\Delta V/V_0 = 38{\cdot}54 \times 10^{-7}p - 39{\cdot}2 \times 10^{-12}p^2 \text{ at } 30^\circ$$
$$\text{and} = 38{\cdot}64 \times 10^{-7}p - 35{\cdot}8 \times 10^{-12}p^2 \text{ at } 75^\circ$$

These values agree with those given[38] for low pressures at 0°: $-\Delta V/V_0 = 37{\cdot}7 \times 10^{-7}p$. In these measurements, the similarity to calcite has again been stressed, and the anisotropy is further exemplified in magnetic investigations.[39] The diamagnetic susceptibilities, which do not vary from the temperature of liquid nitrogen to room temperature,[40] and rise only slightly on solution in water,[41] are:-[42]

$$\left.\begin{array}{r} \text{parallel to trigonal axis: } 29{\cdot}5 \times 10^{-6} \\ \text{perpendicular to trigonal axis: } 24{\cdot}1 \times 10^{-6} \end{array}\right\} \Delta\chi = 5{\cdot}4 \times 10^{-6}$$

In a further investigation a value of $\Delta\chi$ of $4{\cdot}7 \times 10^{-6}$ is compared with the similar anisotropic difference in molecular refractions where $R_0 - R_e = 4{\cdot}83$[43] or 4·86.[9] Calcite has an anisotropic difference in molecular refraction of 2·99, despite its similar molecular volume: the disparity is believed to be due to the different distances of the oxygen atoms from the central atom of nitrogen (1·09 A.) or carbon (1·24 A.). The birefringence of sodium nitrate has been examined from the standpoint of its possible application to the manufacture of Nicol prisms, but the relatively small values of refractive index for the ordinary (1·5854) and extraordinary (1·3369) rays make the use of sodium nitrate alone impracticable,[44] although such prisms have been successfully applied in conjunction with two glass plates.[45] The birefringence and its temperature variation have been treated theoretically[46] and the phenomenon has been employed for the examination of lattice oscillations.[47] The ultra-violet absorption spectra of crystals[10] and solutions of sodium nitrate have been studied and compared over the range 20 to 300°K.;[48] in a mixture of 1:1 $Na^{15}NO_3$ and $Na^{14}NO_3$ two sharp infra-red absorption peaks appear at 836·1 and 814·4 cm.$^{-1}$ as is expected from theoretical considerations.[49] The following room-temperature Raman spectral lines, all due to nitrate ion, have been reported for crystals of sodium nitrate: 1069 cm.$^{-1}$, becoming 1066 at 280°;[50] 723, 1069,1385;[51] 726,1071,1389,1670, becoming 721,1049,1361 and 1683 respectively in solution.[52] The similarity of the lines with those of solutions of the salt has been pointed out,[53] and the variation of their intensity with temperature[54] and with angle of incidence of the radiation[55] have been studied. The Raman spectra of the supposedly eutectic mixtures of sodium and potassium nitrate have been examined.[56] The Raman effect in incident *X*-ray reflection[57] shows an infra-red active frequency of 200 cm.$^{-1}$.[58] Lattice oscillations account for the diffuse spot pattern of reflected *X*-rays at different temperatures.[59,60]

The dielectric constant of 6·85 (at 18° and 1800 m. wave-length) has been redetermined.[61] Electrical birefringence in many salts, including sodium nitrate, has been investigated.[62] Electrolysis of sodium nitrate crystals leads to alkalinity at the cathode attributable to ion movement by replacement through the lattice or between irregularities[63] and not to displacement of ion columns,[64] in agreement with polarization electromotive force and space-charge measurements.[65,66] Emission of ion rays is said not to occur below the melting point of sodium nitrate.[67]

During the gradual transition occurring between 150° and 275° the variation in thermal expansion is discernible only along the *c* axis,[68] and the expansion characteristics at room temperature accord with Mendelyeev's equations.[69] Along the axis of symmetry $a_3 - a_0\ (1 + 7{\cdot}53 \times 10^{-5}t + 2{\cdot}56 \times 10^{-7}t^2)$; perpendicular to the axis, $a_1 = a_0'\ (1 + 8{\cdot}8 \times 10^{-6}t + 2{\cdot}7 \times 10^{-8}t^2)$; where, at 20°, a_1 is 5·060 A. and a_3 is 16·784 A., and t is the temperature.[70] The coefficients of expansion used in the determination of molecular volume at absolute zero[35] are: $\alpha_{-78 \rightarrow 23}$ 10×10^{-5}; $\alpha_{-190 \rightarrow -78}$ 9×10^{-5} and $\alpha_{-273 \rightarrow -190}$ 4×10^{-5}. The entropy of sodium nitrate at 298·16°K. is given[71] as 27·87 ± 0·08 g.-cal.deg.$^{-1}$ mol.$^{-1}$

The effect of **solid** sodium nitrate on the improvement of grain-growth of alumina at high temperature,[72] on the acceleration of the aragonite → calcite transformation[73] and on the physical properties of calcined gypsum have also been studied.

Attention has been given to the crystallization of fused sodium nitrate,[11] and it has been demonstrated that only impurities, such as potassium acetate and propionate, which considerably reduce its surface tension, produce any marked difference in the behaviour of the pure salt by causing a greater degree of dispersion of crystal aggregates.[75] Most other salts, including sodium nitrite,[76] have very little effect on the surface tension and, hence, on the crystallization characteristics. Minute quantities of potassium nitrate (0·03%) and ferric nitrate (0·05%) improve the quality of polarizing crystals of sodium nitrate made by extremely slow cooling of the melt: physical tests show the crystals to be flawless, with an interfacial angle of 73° 48′ to 71° 07′.[77] The behaviour of inclusions such as bubbles under the action of heat has been studied[78,79] as has the fusion and recrystallization of 4:1 sodium:potassium nitrate mixtures.[80] Several mechanical properties of mixtures of sodium and lead nitrates have been reported.[81] The use of sodium nitrate as a cryoscopic solvent for simple salts has been investigated;[82] solutions of these salts are almost ideal and only ions that are not common to the melt exert any depressing effect.

Various melting points of sodium nitrate have been reported: 309 ± 0·5°;[83] 304°;[20] 308°.[84] The mechanism of melting, which is regarded as occurring at a relatively low temperature for an inorganic compound, has been studied; the small volume change and viscometric data support the view that association complexes are formed on melting and these contribute an entropy term but do not affect the heat of fusion.[85] This is again supported by the fact that the calculated entropy of dissociation on melting is not reached.[86] The entropy of fusion is given as 6·33 g.-cal.[87]

Liquid Sodium Nitrate.

The densities of alkali nitrates and of binary mixtures with other nitrates have been found to vary almost linearly with temperature.[88] Selected examples are given in Table II:-

TABLE II. - DENSITY OF FUSED SODIUM NITRATE

Temperature, t (°C.)	Density
318	1·904
360	1·876
402	1·848
458	1·810

Such data follow the expression $d = a + bt$, for which the values $a = 2{\cdot}134$ and $b = 7{\cdot}03 \times 10^{-4}$ have been given.[89] The melting points, heats of solution, heats of melting and densities of binary mixtures of sodium nitrate with other salts have been reported.[90]

Refractive index data for fused sodium nitrate are summarized in Table III:-[91,92]

TABLE III. - REFRACTIVE INDEX DATA FOR FUSED SODIUM NITRATE

Temperature or Temperature Range	Density	Wave-length mμ	Refractive Index	Dependence on Temperature
320°C.	1·900	589·3	1·431	$1{\cdot}499 - 2{\cdot}12 \times 10^{-4}t$
360	1·873	589·3	1·423	$1{\cdot}499 - 2{\cdot}12 \times 10^{-4}t$
400	1·847	589·3	1·415	$1{\cdot}499 - 2{\cdot}12 \times 10^{-4}t$
440	1·820	589·3	1·407	$1{\cdot}499 - 2{\cdot}12 \times 10^{-4}t$
316 to 450	-	671	-	$1{\cdot}439 - 0{\cdot}00023(t - 360)$
320 to 440	-	643·9	-	$1{\cdot}479 - 1{\cdot}75 \times 10^{-4}t$
316 to 450	-	610	-	$1{\cdot}448 - 0{\cdot}00016(t - 360)$
320 to 440	-	589·3	-	$1{\cdot}499 - 2{\cdot}12 \times 10^{-4}t$
316 to 450	-	589	-	$1{\cdot}452 - 0{\cdot}00020(t - 360)$
320 to 440	-	579·1	-	$1{\cdot}487 - 1{\cdot}75 \times 10^{-4}t$

continued on following page

TABLE III (continued)

Temperature or Temperature Range	Density	Wave-length mμ	Refractive Index	Dependence on Temperature
316 to 440	-	579	-	$1{\cdot}458 - 0{\cdot}00020(t - 360)$
320 to 440	-	546·1	-	$1{\cdot}483 - 1{\cdot}50 \times 10^{-4}t$
316 to 440	-	546	-	$1{\cdot}464 - 0{\cdot}00019(t - 360)$
316 to 420	-	436	-	$1{\cdot}475 - 0{\cdot}00017(t - 360)$

The molecular refraction is said to be 11·54[93] or 11·53[91] (and independent of temperature) at 589·3 mμ, and 13·46 and 11·89 at 671 and 589 mμ and 336° and 360°C. respectively.[92] It was deduced from the data that sodium nitrate was 64·7% ionized at its melting point.[91] A theoretical treatment gives the value of n_D at the critical temperature as 1·127,[94] in agreement with experimental findings.[95] The Raman effect in molten potassium–sodium nitrate mixtures has been examined.[96] The lattice constant of the quasicrystalline structure of molten sodium nitrate is expanded by 7% as compared with that of solid sodium nitrate, as shown by the *X*-ray diffraction pattern between 315 and 370°C.[97]

The surface tension of the molten salt is summarized in Table IV.[75]

TABLE IV. - SURFACE TENSION OF FUSED SODIUM NITRATE AND THE EFFECT OF CARBOXYLIC ACID SALTS

Temperature	Surface Tension (dynes/cm.) in the presence of		
	Molecular %	Potassium Acetate	Potassium Propionate
560°C.	0	107·5	-
470	0	110·4	-
315	0	119·0	-
315	1	110·4	97·86
315	2	106·4	86·1
315	5	94·9	70·3
315	10	83·6	54·8
315	25	62·7	41·7
315	50	51·5	35·7
315	100	42·0	25·6

Alkali metal halides in concentrations up to 10 molar % affect the surface tension by less than 2 dynes/cm. Sodium nitrite has little effect, and this is nearly proportional to concentration, the surface tension rising from that of the nitrite to 111 and 114 dynes/cm. at 400 and 300°C. respectively.[76]

The viscosity of molten sodium nitrate may be represented by the expression:-[98]

$$\log \eta = \alpha + \beta/T$$

for which the constants $\alpha = 2{\cdot}4652$ and $\beta = 755$ are said to give results conforming to experimental figures.[99] Better is the expression:-[100]

$$\log \eta = A + B/(C + T)$$

where A is $-3{\cdot}43407$, B is 1749·79 and C is 340·16. These constants give almost complete agreement with results of experiment, for example those given in Table V.[101,102]

For several salts, including sodium nitrate,[103] the relationship $\lambda\eta\sqrt{M} = 10{\cdot}5$, where λ is the equivalent conductivity and M the molecular weight, holds at the melting point. From this expression it has been deduced that molten sodium nitrate is completely ionized and dissociated,[103] but on the basis of

TABLE V. - VISCOSITY-TEMPERATURE RELATIONSHIP OF SODIUM NITRATE

Temperature	Viscosity (centipoises)
308°C.	0•0292
328	0•0266
337	0•0253
356	0•0228
388	0•0206
406	0•0177
418	0•0183
495	0•0132

conductivity data from sodium-potassium nitrate melts it has been suggested that dissociation varies with the salt and with temperature.[104]

The molecular conductivity of molten sodium nitrate between 321•5 and 487•3°C. is given by the expression:-[105]

$$\mu_t = 41{\cdot}56 + 0{\cdot}205(t - 300)$$

and data for the specific conductance over a similar temperature range are given in Table VI:-[106]

TABLE VI. - SPECIFIC CONDUCTANCE OF FUSED SODIUM NITRATE

Temperature (°C.)	$\kappa(\Omega^{-1}\text{cm.}^{-1})$
487•1	1•679
429•0	1•462
387•0	1•297
351•9	1•148
315•0	0•899

In this investigation, the equivalent conductivity at 560°C. was found to be 74•9, and the r_C/r_A ratio 0•54. The specific conductance can be related to temperature by the expression:-

$$\kappa = A_\kappa e^{-E_\kappa/RT}$$

for which the parameters A_κ and E_κ for molten sodium nitrate-nitrite mixtures are given in Table VII.[89]

TABLE VII. - PARAMETERS IN THE EXPRESSION $\kappa = A_\kappa e^{-E_\kappa/RT}$

Mole % of Sodium Nitrite	A_κ	E_κ (kg.-cal./mole)
100	13•2	2•60
85	12•6	2•63
70	12•0	2•62
50	11•2	2•62
25	11•7	2•75
0	13•4	3•12

Several investigations have been made into the migration of ions in molten sodium nitrate: it has been demonstrated that in solutions of silver nitrate in sodium nitrate the silver transports more charge than the sodium, and nitrate none at all.[107] In addition, the transport number of the cations is almost proportional to their molecular fraction, but that of the anion is nearly constant. It is therefore assumed that there are no complex ions present, dissociation is complete, and the cations are structurally similar.[108] Conductivity data for these melts have been given for the range 290 to 370°.[109] The conductivity of cadmium–sodium nitrate melts at 180 to 320° shows the absence of chemical interaction.[110] The diffusion coefficients of silver ions at concentrations of 0·001 and 0·016 mol./litre in equimolecular mixtures of potassium and sodium nitrate are given, respectively, as 8·4 and 4 (× 10^{-5}cm.^{2}/sec.) at 300° and 122° and as 11 (× 10^{-5}cm.^{2}/sec.) at 400°C.[110] A fused mixture of lithium, potassium and sodium nitrates and potassium chloride at 160° has been examined as a polarographic medium.[112] The density, viscosity and conductivity of molten potassium nitrate–sodium nitrate mixtures have been investigated: temperature coefficients are straight-line functions.[113] Data for the electromotive force across a molten sodium nitrate to glass interface have been published for the temperature range from the melting point to 430°C.; the figures are markedly influenced by the nature of the glass.[114]

Heat capacity curves of mixtures of salts that include sodium nitrate are said to resemble those of glasses. Table VIII presents heat capacity data for several salt mixtures.[115,116]

TABLE VIII.- SELECTION OF HEAT CAPACITY DATA FOR CERTAIN FUSED SALT MIXTURES

Constituents (%)				Heat Capacities (kg.-cal./kg./deg.)	Melting Point (°C.)
$NaNO_3$	$NaNO_2$	KNO_3	$Ca(NO_3)_2$	(Temperature in parenthesis)	
100	–	–	–	0·455 (402·5°); 0·426 (500°)	
45·1	54·9	–	–	0·303 (110°); 0·581 (234·8°); 0·458 (492·5°)	225
45·7	–	54·3	–	0·287 (110°); 0·429 (230°); 0·353 (501·5°)	224
7	40	53	–	0·448 (110·6°); 0·500 (136·0°); 0·418 (503°)	142–148
18	28·5	53·5	–	0·284 (110°); 0·467 (173·7°); 0·394 (502°)	170
54·9	–	–	45·1	0·281 (103°); 0·436 (225°); 0·387 (401°)	–
11·3	–	44·9	43·8	0·361 (123·5°); 0·356 (191·5°); 0·373 (400·5°)	–

In Table VIII, data are given for the extremes of the temperature range measured, and for the temperature corresponding to a maximal or minimal value.

Enrichment of radium by crystallization from sodium nitrate with barium[117] or calcium[118,119] nitrate melts has been considered.

The vapour of sodium nitrate has been examined spectrographically under high vacuum; no complete molecules could be detected, contrary to the finding of unionized molecules of potassium and silver nitrates under similar conditions.[120]

Solutions of Sodium Nitrate.

Various aqueous solubility determinations have been made in the course of physicochemical investigations on sodium nitrate. The data for solubility in water presented in Table IX are selected from several sources.[20,121-124]

A saturated solution of sodium nitrate is said to boil at 120·1°C.[123] The temperature coefficient of solubility has been studied theoretically and compared with that of other 1:1 electrolytes and those of 1:2 and 2:2 electrolytes.[125]

Nitric acid reduces the solubility of sodium nitrate according to an

TABLE IX. - SOLUBILITY OF SODIUM NITRATE IN WATER

Temperature (°C.)	% $NaNO_3$	g.$NaNO_3$/100g. of solution	g.$NaNO_3$ per g.H_2O	mol. $NaNO_3$ per mol.H_2O	g.$NaNO_3$/100g. of water
-17·7	-	-	-	-	60·8
0	-	42·3	-	-	-
16·2	-	-	-	-	84·86
20·0	-	-	-	-	87·81
21	-	-	-	-	88·75
22	-	-	-	-	89·6
23	-	-	-	-	90·4
24	-	-	-	-	91·2
25	-	47·9	-	-	92·1
50	-	53·3	-	-	-
75	-	58·6	-	-	-
94·05	-	-	1·6590	0·3516	-
100	58·25	63·7	-	-	-
102	64·1	-	-	-	-
118	-	67·4	-	-	-
131	70·1	-	-	-	-
151·60	-	-	2·8553	0·6051	-
163	76·2	-	-	-	-
198	82·7	-	-	-	-
201·60	-	-	5·0862	1·0779	-
227	88·3	-	-	-	-
251	92·2	-	-	-	-
253·55	-	-	12·4880	2·6465	-
270·00	-	-	19·262	4·0822	-
275	96·0	-	-	-	-
291	97·6	-	-	-	-
295·35	-	-	58·289	12·353	-
(308)	(100)	-	-	-	-

exponential law, with minima in the solubility-temperature curves at approximately 15° and 75°C. at many concentrations of nitric acid.[126] Solutions saturated with both sodium nitrate and ammonium dihydrogen phosphate contain, respectively, 1·5% and 51·4% at 0°C. and 1·2% and 64·1% at 20°C.[127] Hydrogen peroxide reduces the solubility of sodium nitrate in an exponential manner similar to the effect of nitric acid, the solubility falling from approximately 10 to 4 moles of sodium nitrate per 1000 g. of water on increasing the hydrogen peroxide mole fraction from 0·0 to 1·0[128] at 5°C. Sodium carbonate also decreases the solubility.[129]

The sodium nitrate-water eutectic is given as -18·7°[130] or -17·7°C.,[123] and this transition point, given as a freezing point of -18·5°[131] has been suggested and investigated as a basis for cryoscopic determinations; it is claimed to be suitable for determinations on ions not common to the components of the transition, since these alone affect the freezing point, and the depression is slow and proportional to concentration.

Supersaturated aqueous solutions of sodium nitrate are readily formed and are fairly permanent, although it has been said that spontaneous crystallization occurs at 42°.[132] The supersaturation, ρ, is defined as:-

$$\rho = \frac{c - c_0}{c_0}$$

and is related to temperature by:-[133]

$$\rho = Ae^{B/T}$$

where A and B are constants. In the first approximation:-

$$\rho = \beta\frac{d(\log_e c_0)}{dT}$$

where β is a function of temperature which is the same for all salts. At 20°C., ρ is 0·074 (calculated[133,134]) or 0·064 (experimental[133]). The value of ρ is in accord with the lack of hydration. The supersaturated solutions have been studied dilatometrically,[135] viscometrically[136] and by means of vapour pressure:[137] no irregularities occurred at saturation or 'temperature of spontaneous crystallization' points on the smooth volume- or viscosity-temperature curves. The shape of crystals from supersaturated solution has been shown to be independent of temperature, but varies slightly with the degree of supersaturation and, hence, with viscosity of the solution, high values of viscosity leading to the formation of needle-shaped crystals.[138]

The crystallization of sodium nitrate from aqueous solution in the presence of other materials has been examined: very slight or negligible changes of crystalline form by simple organic compounds[139-141] have been reported, but organic dyes are said to have a greater, but still minor, effect by preventing lattice building,[142,143] although this effect is insufficient to prevent caking of the crystals. Adsorption of dyes is said to be interstitial and is selective on the $V_{1,1,1}$ crystal faces.[144] The creep on glass surfaces of sodium nitrate crystals from saturated solution,[145] and the adsorption of sodium ions on quartz from sodium nitrate solutions[146] have also been studied. The closing of fissures in sodium nitrate crystals has been shown to commence immediately on contact with its solution.[147] The crystallization from water in the presence of potassium nitrate has been examined in the course of systematic investigation of the crystallization of binary eutectics[148,149] under different conditions, and in a search for a rapid analytical method for sodium, as nitrate, in potassium nitrate by radioactive assay.[150]

The vapour pressure of solutions of sodium nitrate has been exhaustively investigated. Table X presents vapour pressure, density and partial molal volume data for solutions over a range of molarity and molality.[151]

TABLE X. - DENSITY AND VAPOUR PRESSURE OF SOLUTIONS OF SODIUM NITRATE AT 25°

Molality	Molarity	Density(d_4^{25})	Vapour Pressure (mm.Hg)	Partial Molal Volume	Activity of Solvent
0·0	0·0000	0·997074	23·752	-	1·0000
0·2	0·1983	1·008245	23·596	28·749	0·9934
0·4	0·3942	1·019128	23·446	29·151	0·9871
0·6	0·5878	1·029723	23·299	29·552	0·9809
0·8	0·7791	1·040108	23·152	29·857	0·9747
1·0	0·9680	1·050308	23·006	30·100	0·9686
2·0	1·8778	1·098511	22·332	31·076	0·9402
4·0	3·3523	1·183332	21·092	32·369	0·8880
6·0	4·9875	1·255220	19·999	33·344	0·8420
8·0	6·2729	1·317351	18·987	34·048	0·7994
10·83	7·8457	1·391372	17·554	34·851	0·7391

The vapour pressure of saturated aqueous solutions of sodium nitrate can be represented by the expression:-[152]

$$p/p_W = 0{\cdot}7873 - 0{\cdot}00220t - 0{\cdot}0000014t^2$$

where p is the vapour pressure of the solution at t°C. and p_W is that of water at the same temperature between 10 and 150°. Other investigations[121,153] have been made, and from them the data given in Table XI have been selected.

TABLE XI.- VAPOUR PRESSURE OF SATURATED SOLUTIONS OF SODIUM NITRATE

Temperature (°C.)	Vapour Pressure (mm. Hg)
19·0	12·34
20·0	13·06
21·0	14·02
22·0	14·87
23·0	15·76
24·0	16·70
25·0	17·68
26·0	18·72
28·0	20·96
30·0	23·46

Solutions saturated with respect to both ammonium and sodium nitrates have the vapour pressures shown in Table XII.[154]

TABLE XII.- VAPOUR PRESSURE OF SOLUTIONS SATURATED WITH BOTH SODIUM NITRATE AND AMMONIUM NITRATE

Temperature (°C.)	Vapour Pressure (mm. Hg)
10	5·4
15	7·0
20	9·0
25	11·6
30	14·6
35	18·5

The following expressions have been found to represent the vapour pressures of the saturated solutions of sodium nitrate mixed with other nitrates:-
(a) for sodium and lead nitrates from 10 to 150°:-[155]

$$p/p_W = 0{\cdot}7710 - 0{\cdot}002209t - 2{\cdot}17 \times 10^{-6}t^2$$

(b) for sodium and ammonium nitrates:-[156]

$$\text{from 10 to } 84{\cdot}2°,\ p/p_W = 0{\cdot}6205 - 0{\cdot}004894t - 3{\cdot}5 \times 10^{-6}t^2$$
$$\text{from } 84{\cdot}2 \text{ to } 121{\cdot}1°,\ p/p_W = 0{\cdot}6026 - 0{\cdot}004976t;$$

the change of direction is due to the transition of γ to δ-ammonium nitrate at 84·2°C.
(c) for sodium, lead and ammonium nitrates:-[157]

$$\text{from 10 to } 84{\cdot}2°,\ p/p_W = 0{\cdot}5833 - 0{\cdot}004807t - 4{\cdot}8 \times 10^{-6}t^2$$
$$\text{from } 84{\cdot}2 \text{ to } 112{\cdot}3°,\ p/p_W = 0{\cdot}6315 - 0{\cdot}006264t + 5{\cdot}7 \times 10^{-6}t^2$$

Vapour pressure measurements have been used to throw light on the nature of sodium nitrate in aqueous solution, but, on the whole, workers reach conflicting conclusions. Thus, an investigation of the Arrhenius i factor by means of osmotic and vapour pressure measurements led to the conclusion that hydrated undissociated molecules were present in solution.[158] Incomplete dissociation is postulated to account for low experimental activity coefficients[159] in agreement with heat of dilution measurements.[160] Again, since it is assumed that the nitrate ion is not hydrated, it may associate instead with an undissociated molecule of sodium nitrate to account for certain cryoscopic results.[161] The assumption that the salt is not hydrated,[162] is supported on grounds of molal volume data:[151] on the other hand, partition experiments indicate that 11·1 molecules of water are 'immobilized' by one molecule of the salt,[163] in agreement with other cryoscopic measurements indicating that 11·1 molecules of water are associated with one of sodium nitrate in 0·5M. solution and 9·3 in 1·0M. solution respectively.[164] From thermal data it has been deduced that the number of water molecules in a 'frozen' solvent envelope is 14, of which 8 (expanded relative to pure water) are associated with the nitrate ion and 6 (compressed relative to water) with the sodium ion.[165] Hydration has also been invoked to explain the non-linearity of the relationship between the square root of the concentration and the molar energy of interaction of the ions[166] and the decrease of the compressibility of water upon dissolution of sodium nitrate in it, as determined ultrasonically.[167] A comprehensive survey of the literature, especially that relating to vapour pressure lowering and the conductivity of sodium nitrate in water, leads to the conclusion that sodium nitrate is associated with 8 molecules of water, all attached to the sodium ion.[168]

The ionic radii in saturated solution have been determined as: $r_{NO_3'} = 2{\cdot}43 \times 10^{-8}$ and $r_{Na^{\cdot}} = 1{\cdot}07 \times 10^{-8}$ cm. The values are smaller than those for dilute solutions, but larger than those in the solid material.[169]

The heat of dilution of sodium nitrate is −1870,[130] −1970[170] and −2130[170,171] g.-cal./mol. at −18·7° (eutectic), 0° and 16°C., respectively. The heat of dilution of dilute (<0·1N.) solutions of sodium nitrate has been examined analytically,[121] and is given by the expressions:-[160,172]

$$\text{Integral heat of dilution, } V_m = 297\sqrt{m} \text{ or } 320\sqrt{m},$$

where m is the concentration in g.-mol./litre. The relative apparent heat content and the relative partial molal heat content have been determined at 18°C., and representative data for these, together with the molal heat content of the water in the solution, are given in Table XIII.[173]

TABLE XIII. - THERMAL DATA FOR SOLUTIONS OF SODIUM NITRATE

Concentration (mole/litre)	Relative apparent heat content (g.-cal.)	Relative partial molal heat (g.-cal.)	
		For sodium nitrate	For water
0·0025	20	30	−0·00045
0·01	32	39	−0·0013
0·09	9	−34	+0·068
0·25	−71	−208	+0·617
1·00	−475	−942	+8·42
1·96	−868	−1582	+25·28

The apparent molal heat capacity and partial molal heat capacity, ϕ_c, from 18 to 25°C. is given by the expression:-[174]

$$\Phi_c = \Phi_c^0 + 20{\cdot}0m^{\frac{1}{2}}$$

where Φ_c^0 is −12·6 g.-cal., varying with temperature according to the expression $\frac{d\Phi_c^0}{dT} = \frac{2{\cdot}0}{7}$ g.-cal. mol.$^{-1}$ deg.$^{-1}$, and m is concentration in moles/1000 g. of water. The specific heat at 21°C. is 0·689 for a solution containing 90·00 mole of sodium nitrate per 1000 moles of water.[175] Thermal expansion measurements have been made on concentrated solutions up to 90°C.[176]

The refractive indices and equivalent – *i.e.*, molecular – refractivities of aqueous solutions of sodium nitrate have been determined and some of the values are given in Table XIV.[177,178]

TABLE XIV. - REFRACTIVE INDICES OF AQUEOUS SODIUM NITRATE SOLUTIONS

Concentration (g.-eq./l.)	Density d_4^{25}	Refractive Index $n_{\mathrm{D}_3}^{25}$	Equivalent Refractivity $R_{\mathrm{D}_3}^{25}$
0	0·99707	1·33259	(11·21, extrapolated)
1·7629	1·08754	1·34710	11·197
4·6610	1·20835	1·36501	11·183
6·6176	1·27547	1·37434	11·170
9·1926	1·35045	1·38427	11·157

From the equivalent refractivity of the salt, that of the ions was found to be: $R_{\mathrm{Na}^{\cdot}}$, 0·200 and $R_{\mathrm{NO}_3{}'}$, 11·01. The temperatures of maximum refractivity of the solutions are: 0·5N., −11·0°; 0·025N., −6·8°C.[179]

The ultra-violet absorption at 3000A. of solutions of sodium nitrate[11] has been observed in the plane of the nitrate ions in the crystal state, and a periodicity of infra-red, but not ultra-violet, absorption with dilution has been reported.[180] Investigation of the Raman spectrum has given the following values of $\backslash\nu$(cm.$^{-1}$): 1048, 720;[181] 1683, 1361, 1049, 721;[52] 1357, 1049, 725;[182] 1042, 700;[183] 1064.[184] The displacements of 720 and 1048 cm.$^{-1}$ are due to the nitrate ion. It appears unlikely that any unionized molecules are present even in concentrated solutions.[182]

Electrical conductivity measurements on aqueous solutions are summarized in Table XV.[185]

TABLE XV. - CONDUCTIVITY DATA FOR AQUEOUS SODIUM NITRATE

Litres of solution containing 1 mol. of sodium nitrate	Equivalent conductivity		Concentration (mol./l.)	Equivalent conductivity	
	18°	100°		18°	100°
1284	103·25	333·4	0·001	102·9	332·0
1033	103·0	332·1	0·002	101·9	327·0
397·0	101·5	326·5	0·005	100·1	321·0
129·5	99·02	316·7	0·01	98·2	313·0
59·47	96·38	306·3	0·02	95·7	303·0

Hence, by extrapolating and using other data, the equivalent conductivities at infinite dilution are: Λ_0(18°), 105·1 and Λ_0(100°), 339·0, and for the individual ions:

	0°	18°	100°
$l_{\mathrm{Na}^{\cdot}}$	26·1	43·2	152·0
$l_{\mathrm{NO}_3{}'}$	40·0	61·8	186·5

Conductivity measurements lead to the conclusion that sodium nitrate is not completely dissociated,[186] in agreement with activity and osmotic coefficient determinations.[159] Thus, for 25°C., the following figures have been published:-

Molality	0·01	0·05	0·1	0·5	1·0
α	0·996	0·985	0·982	0·947	0·913
K	2·0	2·0	3·0	3·2	2·9
ψ'	0·978	0·943	0·912	0·898	0·880

where $\alpha = \dfrac{\Lambda_{\text{observed}}}{\Lambda_{\text{calculated}}}$, the dissociation constant $K = \dfrac{\gamma^2\alpha^2 c}{1-\alpha}$, γ is the limiting activity coefficient, c is concentration and ψ' is the calculated osmotic coefficient. The conductivity and viscosity of these solutions have been treated theoretically,[187] and the conductivity at $4{\cdot}39 \times 10^7$ has been demonstrated to be almost unchanged from that at low frequencies.[188] The Soret coefficient for 0·001N. to 0·004N. solutions of sodium nitrate is $1{\cdot}7 \times 10^3$ units per degree,[189] compared with the calculated value of $3{\cdot}2 \times 10^3$ units.[190]

Cataphoresis in sodium nitrate solutions requires a cathode current density of 0·2 to 0·5 milliamp./cm.^{2} and a potential gradient of 0·4 to 0·5V./cm. for crystal deposition at the cathode.[191] The formation of anodic arcs in sodium nitrate solutions has also been studied.[192]

Equivalent conductivities of 0·0001 to 0·002N. solutions in liquid hydrogen cyanide are given by the expression:-[193]

$$\Lambda_c = 333{\cdot}8 - 250c^{1/2} \text{ at } 18^\circ$$

with $l_{0\mathrm{Na}^{\cdot}}$ 132·4 and $l_{0\mathrm{NO}_3'}$ 201·4. Since the ionic mobilities are found to be in the unusual order: $\mathrm{Na} < \mathrm{Li}^{\cdot} < \mathrm{K}^{\cdot} < \mathrm{Rb}^{\cdot} < \mathrm{Cs}^{\cdot}$, it is concluded that solvation in hydrogen cyanide is less than in, e.g., water, and that ionization is complete. The product $l_0\eta$ is normal for nitrilic solvents (for $\mathrm{Na}^{\cdot}$, 0·27; for NO_3', 0·40). Table XVI gives conductivity data for sodium nitrate in dimethylformamide[194] and ethylenediamine.[195] The dissociation constants are, respectively, 0·023 and 0·0001120 in these solvents.

TABLE XVI. - EQUIVALENT CONDUCTIVITY OF SODIUM NITRATE IN DIMETHYLFORMAMIDE AND ETHYLENEDIAMINE

Dimethylformamide	25°C.	Ethylenediamine	25°C.
G.eq./litre	Equivalent Conductivity	Molarity	Equivalent Conductivity
0·0000945	84·9	0·00005574	57·87
0·0006778	81·2	0·0001503	48·39
0·001422	78·0	0·0004403	35·34
0·002872	73·7	0·0009567	26·95
0·003964	71·3	0·001288	24·36
(0, by extrapolation,)	87·2	(0, by extrapolation,)	75·1

The dielectric constant at 50 to 2200 cycles per sec. varies with concentration of sodium nitrate showing a minimum at approximately 0·01M.[196,197] and it has been suggested that the number of molecules of water per unit ionic charge and per molecule of electrolyte are $5{\cdot}3 \times 10^3$ and 124 respectively at the minimum values of the dielectric constant. This sheath of water is composed of oriented dipoles and becomes small at high frequencies. The expression:-

$$D = D_0(1 + 0{\cdot}051c^{1/2} - 1{\cdot}1c)$$

is stated[198] to describe the change of dielectric constant, D, with concentration, c, below 0·001M. Complex ions have been proposed to account for the minima in the concentration curves.[199] An alternative expression:-

$$D = D_0e^{-\mu},$$

where μ is a function of the number of ions per molecule, of ionic radius, and of concentration, ionic valencies, compressibility of the solute and crystallography of the solvent, has been proposed and criticized.[200]

The single potential of the boundary between sodium nitrate in water and in amyl alcohol is +13·1mV.[201] Sodium nitrate coagulates completely a large number of organic and inorganic colloids, including basic lead acetate, ferric chloride, and blood protein, without chemical action,[202] and its effects on the precipitation of silver thiocyanate and silver iodide,[203] of aerosols[204] and of ethylhydroxyethylcellulose solutions[205] have been investigated. The primary salt effects in colloidal electrolytes such as long-chain alkanesulphonates,[206] alkylbenzenesulphonates,[207] and other surface active agents[208] have also been studied.

The diamagnetic susceptibility of sodium nitrate solutions varies linearly with concentration, the gram ionic susceptibility being $-20{\cdot}1 \times 10^{-6}$ [209] The diamagnetic double refraction of a solution containing 42g. of sodium nitrate per 100 c.c. of solution at 17·1° is +0·11° and the Cotton-Mouton constant is $+0{\cdot}99 \times 10^{-14}$. This leads to a figure of $1{\cdot}32 \times 10^{-14}$ for the solid salt.[210] Whereas the diamagnetic resonance of the nitrate ion is identical in ammonium and sodium nitrates, that in nitric acid is different and varies linearly with concentration.[211]

In the course of an investigation into the rate of evaporation of sodium nitrate solutions, surface tension and viscosity data were obtained at 80°C., some of which are given in Table XVII.[212]

TABLE XVII. - SURFACE TENSION AND VISCOSITY OF SOLUTIONS OF SODIUM NITRATE

Concentration of Sodium Nitrate (%)	Density d^{20}	Viscosity η^{80}	Surface Tension γ^{80}(dynes/cm.)
12·5	1·085	0·0040	64
25·5	1·185	0·0053	67
36·0	1·280	0·0066	70
45·5	1·372	0·0091	73
54·0	1·45–	0·0132	–

The surface tension has also been treated theoretically.[213]

Solutions of sodium nitrate in concentrations up to 0·6M. display no ultrasonic dispersion at 2000, 6000 and 10,000 cycles and the absorption follows the relationship:-[214]

$$c = \beta . \alpha / \nu^2$$

where c is molarity, α is absorption coefficient, β is a proportionality constant and ν is the velocity of sound. For sodium nitrate, β is positive, although it may be slightly reduced at high concentrations. The effect of ultrasonic beams on solutions of sodium nitrate during electrolysis shows that the adiabatic compressibility is reduced and the velocity of sound is increased at all concentrations of the salt; further, the electrical resistance of the solution is increased and the apparent molar compressibility is negative, following the Gucker linear equation.[215]

The influence of sodium nitrate on the properties of 100% nitric acid has been investigated: 1000 g.-cal. are evolved on dissolution of 1 g. mol. of the salt in a large volume of acid, with formation of independent ions, as shown by the Raman spectrum; the vapour pressure of the system falls rapidly with increasing concentration of sodium nitrate, presumably owing to complex ion formation. This supposition is borne out by the decrease in nitric acid vapour pressure, but not in that of water, in similar experiments on 80% aqueous nitric acid.[216] The salting out of iodine from dilute nitric acid solutions by sodium nitrate may be represented by a formula of the type:-[217]

$$S = S_0 e^{-kc}$$

where S_0 is the solubility of iodine in water, S is the solubility in a sodium nitrate solution of concentration c g.-mol. per 1000 g. of water, and k is a constant depending on the nature of the salt and the presence of other ions. Thus k is 0·0533 in water, 0·0577 in 1·3N-nitric acid, and 0·0593 in 2·7N-acid. The salting out effect of sodium nitrate on benzoic and phenylacetic acids[218] has been shown to be very similar for both acids, the parameters decreasing slightly with increasing temperature. The salting-out effect on ethyl acetate[219] (see Table XVIII) and various other organic substances[220] has also been examined.

TABLE XVIII. - SALTING OUT OF ETHYL ACETATE BY SODIUM NITRATE

Temperature (°C.)	Molarity		S_0/S
	Sodium Nitrate	Ethyl Acetate	
25	1·0	0·7058	1·166
	0·75	0·7395	1·118
	0·5	0·7740	1·076
	0·25	0·8010	1·047
	0	0·9957	-
35	1·0	0·6246	1·185
	0	0·7591	-

The solubilities of silver propionate and butyrate,[221] of arsenious oxide,[222] of nickelous hydroxide,[223] of lead sulphate[224] and of cadmium and manganese oxalates[225] increase almost linearly with increasing ionic strengths of sodium nitrate, indicating that no complex ions are formed; the extraction of uranyl ions from sodium nitrate solutions with 2-thenoyltrifluoroacetone similarly shows no complex ion formation with sodium nitrate.[226] On the other hand, the solubility of silver chloride increases markedly, presumably owing to complex formation with the silver ion in increasing ionic strengths of sodium nitrate.[227] The effects of constant or regulated ionic strengths, supplied in the form of sodium nitrate, on the rates of decomposition of hypochlorous acid,[228] the rates of hydrolysis of allyl halides,[229] of methyl propionate[230,231] and of ethyl formate,[232] on the degree of ionization of acetic acid[233] and on the acidity function[234] ($y = \log C_{H^{\cdot}} + pK_a + L\mu$, where L is a constant and the other symbols have their usual significance) have been investigated. Sodium nitrate has been taken as an example in the studies of the theory of ion-exchange materials[235,236] and of diffusion processes in soils.[237] The effect of sodium nitrate on the dissociation constant of acetic acid[238] and its cryoscopic lowering of the sodium sulphate decahydrate → sodium sulphate transition point[239] is normal. The effects of sodium nitrate on the supercooling of water[240] and on the vapour pressure of system ethanol–water[241] have also been investigated.

Sodium nitrate exerts a negligible effect on the electrophoresis of silver iodide sols[242] and uranyl ions,[243] and it does not appear to produce an 'isozeonic' effect (whereby at a certain concentration one salt ceases to affect the b.p. of a solution of another salt) in solutions of cobalt chloride, glucose or calcium nitrate.[244] During electrolysis of dilute potassium permanganate solutions in the presence of sodium nitrate at 280 V., the potassium ions associate with those of nitrate and permanganate ions with those of sodium during their migration;[245] the effect has been studied up to 1500 V.[246] Polarization of aluminium in sodium nitrate solutions shows that the anion is ineffective in influencing the nature of the cathodic oxide film, but anodic areas were highly polarizable by the sodium nitrate solution.[247] Sodium nitrate has been demonstrated to be anionophilic with respect to collagen.[248] Decomposition of hydrogen peroxide in the presence of sodium nitrate, *inter alia*, has been studied.[249]

Solutions of sodium nitrate in non-aqueous solvents have proved of interest. Conductivity measurements in liquid hydrogen cyanide,[193] dimethylformamide[194] and ethylenediamine[195] have already been mentioned; Table XIX gives solubility figures for sodium nitrate in glacial acetic acid.[250]

TABLE XIX. - SOLUBILITY OF SODIUM NITRATE IN ACETIC ACID

Temperature (°C.)	Concentration (%)
27·0	0·122
36·0	0·166
46·5	0·202
53·7	0·246
78·5	0·448
93·4	0·641
103·0	0·854

In liquid monomethylamine[251] from 0° to 25°C., density and apparent molal volume can be calculated from the formulae given in Table XX, in which *c* is concentration in g./ml. The absence of solvates in these solutions is reported.

TABLE XX. - FORMULAE FOR EVALUATION OF DENSITY AND APPARENT MOLAL VOLUMES OF SODIUM NITRATE IN MONOMETHYLAMINE

Temperature (°C.)	Density	Apparent Molal Volume
0	$0{\cdot}68667 + 0{\cdot}07429c - 0{\cdot}00495c^{3/2}$	$17{\cdot}45 + 3{\cdot}2508c^{1/2} + 2{\cdot}0660c$
10	$0{\cdot}67464 + 0{\cdot}07636c - 0{\cdot}00559c^{3/2}$	$14{\cdot}80 + 3{\cdot}8672c^{1/2} + 2{\cdot}3715c$
18	$0{\cdot}66490 + 0{\cdot}07752c - 0{\cdot}00569c^{3/2}$	$13{\cdot}42 + 4{\cdot}2635c^{1/2} + 2{\cdot}0986c$
25	$0{\cdot}65623 + 0{\cdot}07778c - 0{\cdot}00520c^{3/2}$	$12{\cdot}32 + 4{\cdot}9056c^{1/2} + 1{\cdot}6339c$

In liquid ammonia, sodium nitrate has the following solubilities: at 0°C., 56·05g./100g. of solution;[252] at 25°C., 97·60g./100g. of solution or 58·95g./100ml. of solution.[253] The effect of sodium chloride on the solubility of sodium nitrate in liquid ammonia has been investigated, and data are presented in Table XXI. It was concluded that the common ion effect, and hence ionization, could operate in these solutions.[254]

TABLE XXI. - SOLUBILITY OF SODIUM NITRATE IN LIQUID AMMONIA IN THE PRESENCE OF SODIUM CHLORIDE

Concentration of Salt (mol. per 10 mol. of ammonia)	
Sodium Chloride	Sodium Nitrate
0·0	1·95
0·0524	1·80
0·0686	1·694
0·0746	1·232
0·087	0·46
0·088	0·0

The univariant points in the vapour pressure of liquid ammonia containing sodium nitrate, with excess of solid salt present, are given in Table XXII,[255,256] and the density and vapour pressure data for sodium nitrate solutions in liquid ammonia that have been reported[257] are recorded in Table XXIII. This lowering of the vapour pressure has been suggested as a means of facilitating the storage of liquid ammonia.[258]

TABLE XXII. - UNIVARIANT TEMPERATURE-VAPOUR PRESSURE POINTS FOR THE SYSTEM LIQUID AMMONIA-SODIUM NITRATE

Temperature (°C.)	Vapour Pressure (mm.Hg)	Temperature (°C.)	Vapour Pressure (atmospheres)
−35·0	325	0	2·20
−30·7	400	4	2·65
−26·0	500	13	3·63
−22·1	600	16	4·20
−16·7	760	20	4·95
−15·6	800	25	6·05
−10·3	1000	30	6·85
− 6·3	1200		

TABLE XXIII. - DENSITY AND VAPOUR PRESSURE LOWERING DATA FOR SOLUTIONS OF SODIUM NITRATE IN LIQUID AMMONIA

Concentration (g. $NaNO_3$ per 100 g. NH_3)	Density d_4^{15}	Concentration (g.mol. $NaNO_3$ per 1000g.NH_3)	Lowering of Vapour Pressure (mm.Hg)
0	0·6182	0·229	22
4·16	0·643	0·981	84
31·00	0·781	2·525	233

During the isothermal evaporation of a saturated solution at −20°, 5·4 kg.-cal./g.mol. are absorbed, and whereas the true molar heat of solution of sodium nitrate in liquid ammonia is 3600 g.-cal. at −33·4°,[259] in a saturated solution the heat of solution is said to be small.

The decomposition potential of sodium nitrate in liquid ammonia is given as 2·52V. (cf. 2·15V. in water),[260] and the specific conductivities of saturated solutions at various temperatures are given in Table XXIV.[256]

TABLE XXIV. - SPECIFIC CONDUCTIVITY OF SOLUTIONS OF SODIUM NITRATE IN LIQUID AMMONIA AT VARIOUS TEMPERATURES

Temperature (°C.)	Specific Conductivity (mho)
−16	0·0768
−15	0·0768
−7	0·1107
0	0·1269
+3	0·1400
+10	0·1565
+15	0·1649
+19	0·1711
+30	0·1776

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Chemical Properties of Sodium Nitrate

This section is confined as far as possible to the specific chemistry of sodium nitrate, omitting chemistry that is merely exemplified by the case of sodium nitrate and the chemistry of sodium and nitrate ions supplied incidentally as sodium nitrate.

The thermal decomposition:-

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

has been shown to have a dissociation temperature of 528•5° at standard pressure,[1] and the heat of reaction is calculated to be −43•7 kg.-cal. compared with the experimental value[2] of −46•4 kg.-cal. At 520°C., equilibrium is established in 144 hours with 8% conversion to nitrite, unless impurities such as aluminium, cast iron or stainless steel are present when equilibrium is reached in a shorter time but some reduction, in addition to dissociation, may occur.[3] Sodium nitrite first appears at about 255°C., and at higher temperatures sodium peroxide, detectable at about 750°, and oxide are formed. At a temperature of 900° the salt is completely vaporized. The colour gradually deepens to dark brown as the temperature is raised, and the melt solidifies to a yellow (temperature of heating, 600 to 800°) or colourless(>800°) solid depending on the nature and amount of peroxide present.[4] This has been confirmed,[5] and the peroxide yield has been improved by very rapid heating of the salt to a high temperature: the nature of the peroxide is difficult to establish owing to attack on any containing vessel. The thermal decomposition has

Refs. p. 1255

been followed by means of differential thermal analysis which detected the transition between 150° and 275°, the melting point at 304° and slight changes at 520°, 612°, 710°, 753° and 777° which corresponded to the respective observations of slight bubbling (SB), rapid bubbling (RB), slight nitrous fume (SN) evolution, rapid (RN) and then vigorous (VN) nitrous fume evolution, as shown in Fig. 1.[6] The thermal decomposition is said to be retarded in the presence of 10% by weight of strontium nitrate.[7]

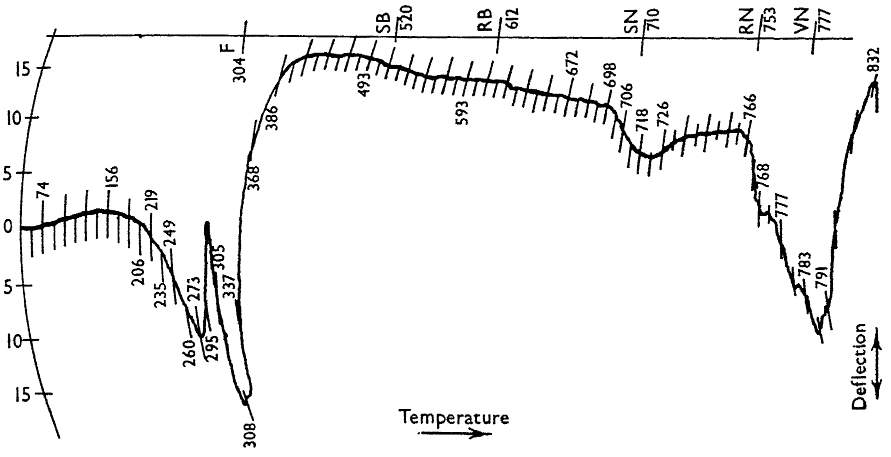


FIG. 1. DIFFERENTIAL THERMAL ANALYSIS OF SODIUM NITRATE

Sodium nitrate dissociates to unspecified products at the crystal surface when illuminated in linearly polarized ultra-violet light, especially when this is incident to the plane of the nitrate ions,[8] and oxygen is evolved, with concurrent formation of sodium nitrite, when the salt is subjected to intense ionizing radiation; the mechanism is believed to be based on electronic excitation.[9] Superheated steam at about 600° largely decomposes sodium nitrate by hydrolysis,[10] and whilst sodium nitrate alone at 1000°C. decomposes with a 19 to 22% yield of nitrogen oxides, in the presence of water vapour this can be increased to 80%; at 800° to 1000° acidic, but not basic, oxides can increase the yield still further to 97–99%.[11]

Reduction of sodium nitrate has been achieved by several agents.

(*a*) Hydrogen in the silent electric discharge yields small quantities of sodium nitrite[12] and possibly some ammonia and ammonium salts,[13] and hydrogen at temperatures above 400° yields sodium nitrite: the latter reaction is accelerated by additions of sodium hydroxide or small amounts of cupric oxide as catalyst, in the presence of which a 95% yield can be obtained in 30 minutes.[14]

(*b*) A slow reduction, accelerated only by large quantities of sodium hydroxide, occurs with carbon monoxide at temperatures above 500°C.[14]

(*c*) Addition of calcium to molten sodium nitrate–sodium nitrite mixtures at 250° reduces the nitrate to nitrite, a 0·75 molar ratio of calcium to nitrate giving the optimum yields while larger quantities lead to reduction of nitrite to nitrogen owing to the catalytic effect of the lime produced in the reaction[15] $NaNO_3 + Ca \rightarrow NaNO_2 + CaO$.

(*d*) A 15% excess of lead converts sodium nitrate completely to nitrite at about 415°, at which temperature the thermal decomposition plays some part.[16]

(*e*) Mixtures of aluminium, zinc or tin with sodium nitrate in the presence of barium hydroxide yield ammonia at the softening point, but if sodium hydroxide replaces barium hydroxide, only nitric oxide is evolved until higher temperatures are reached; nascent hydrogen is said to be here the active reducing agent,[17] although atomic hydrogen leads only to the formation of sodium hydroxide or oxide.[18]

(*g*) Several references have been made to the use of sodium nitrate in the deposition of adherent oxide layers on metals such as iron, cobalt, nickel, copper, chromium and manganese and their alloys:[19-21] in these processes the sodium nitrate is reduced, but nothing has been said as to the nature of the products or of the oxide film. Similar observations have been made on oxide film formation on heating metals such as copper,[22] aluminium alloys (especially when sodium hydroxide is present)[23] and iron[24] with sodium nitrate. In the case of iron the product is magnetite.

(*h*) Sodium nitrate is reduced to unspecified products by carbon, sulphur and possibly silicon when it is added during the open-hearth process for steel-making,[25-29] in the improvement of cast iron[30] and in the casting of metals.[31]

(*i*) On adding sodium nitrate to molten glass any ferrous ions are oxidized to 'colourless iron'[32,33] and any colour due to gold[34] disappears: this has been utilized in reducing the colour of some glasses, but the products of reduction are unknown.

(*j*) Fusion of sodium cyanide with sodium nitrate oxidizes it to sodium cyanate, and this reaction has been used to remove traces of cyanide from the cyanate.[35]

(*k*) Organic material, especially jute used in storage bags, normally causes reduction of sodium nitrate at about 160° and ignition follows at or below 220°C.;[36] on the other hand, no vigorous reaction occurs with sodium salts of fatty acids or sodium thiocyanate at 330° to 400°C., although on stronger heating gas evolution commences.[37]

(*l*) Nitric oxide reduces sodium nitrate to the extent of about 4.5% at 315° according to the equation $NaNO_3 + NO \rightarrow NaNO_2 + NO_2$, and the reverse reaction is rapid and almost complete at 315° to 450°C.[38]

(*m*) In solution the reduction of sodium nitrate by organic material and hydrogen sulphide has been used to purify industrial effluents,[39-42] and the similar oxidation of toxic ferrous ions to ferric ions in soils has been achieved.[43,44]

(*n*) The increase in polarization of steel,[45] iron[46] and aluminium[47] owing to oxide film formation in the presence of sodium nitrate solutions has also been studied.

(*o*) The influence of sodium nitrate on the hydrogen reduction of several oxides has been considered.[48]

The exchange reactions in the reciprocal systems sodium–lithium, sodium–potassium, sodium–rubidium and sodium–caesium nitrates and hydroxides,[49] in sodium–potassium nitrates and bromides,[50] and in sodium–potassium nitrates and fluorides (the latter having a bias towards the potassium nitrate–sodium fluoride pair[51]), and in sodium–potassium nitrates and iodides,[52] have been investigated and the thermal effects evaluated. Fusion of finely ground powders of sodium nitrate and potassium chloride results in a partial conversion to sodium chloride and potassium nitrate.[53] Heating sodium nitrate with alumina, presumably in the form of aluminates, causes evolution of nitrogen oxides.[54] Precipitation of calcium carbonate in the presence of sodium nitrate results in the formation of an inner polar adsorption compound $Na_2CO_3,H_2O,CaCO_3$ due to the reaction:-[55]

$$2NaNO_3 + CO_3'' \rightarrow Na_2CO_3 + 2NO_3'$$

Refs. p. 1255

The reaction of 8N-sodium nitrate with water is said to cause a conversion of trihydrol, $(H_2O)_3$, to monohydrol, H_2O, with little effect on dihydrol;[56] this hypothesis has been supported by the evidence of Raman spectra[57] and has been employed to explain boiling point and adsorption phenomena in sodium nitrate solutions.[58]

The yield of sodium hydroxide during electrolysis of a sodium nitrate solution is not quantitative at the cathode owing to transport of hydrogen ions.[59] A saturated aqueous solution of the salt (500g./litre) containing sodium hydroxide (50g./litre) can be electrolytically reduced at 0·5 amp./cm.^{2} and 2·1 to 2·6V. at about 115°C. during the course of 4 to 6 hours to give an 80% yield of ammonia and a 20% yield of sodium nitrite.[60] Electrolysis of 3, 1 and 0·01M-solutions of sodium nitrate between copper electrodes showed normal dissolution of the anode except in the most dilute solution where an adherent yellow-brown oxidation product was found on the anode.[61]

Studies have been made of the reaction of nitrosyl chloride at 30° to 80°C. with sodium nitrate in the presence of sodium chloride, as saturated aqueous solutions, to yield nitric oxide,[62] and of the conversion of sodium nitrate in concentrated aqueous solution to chloride and also to aqua regia with hydrogen chloride at 35° to 85°C.[63] Sodium nitrate, when applied as a fertilizer, is said to be immediately utilized in part by the plants, with a consequent increase in the pH of the soil and also the production of soluble calcium and magnesium nitrates from colloidal compounds of these elements, the soluble salts being then leached from the soil.[64]

Several reactions of sodium nitrate in liquid ammonia have been studied. The salt reacts with carbon dioxide to give sodium carbamate:-

$$NaNO_3 + CO_2 + 2NH_3 \rightarrow NaCO_2NH_2 + NH_4NO_3$$

which can then be hydrolyzed with sodium carbonate in the presence of water to give further sodium carbonate[65] as an easily worked-up product. Electrolysis at 0·1 amp./cm.^{2} of a liquid ammonia solution at -40° to -47°C. gives, besides nitrogen and ammonium nitrate, 60–65% yields of sodium nitrite together with some sodium hydroxide and hydrogen at the cathode:-[66]

Anode reactions: $NO_3' \rightarrow NO_3 + e$

$6NO_3 + 2NH_3 \rightarrow 6NO_3' + N_2 + 6H^{\bullet}$

Cathode reactions: $Na^{\bullet} + e \rightarrow Na$

$2Na + NO_3' \rightarrow NO_2' + Na_2O$

Hence 6 Faradays correspond to the reaction:-

$$3NaNO_3 + 2NH_3 \rightarrow 3NaNO_2 + N_2 + 3H_2O$$

Experiments at -20° to -30°C. and 3 to 6V.[67] show the anode product to be ammonium nitrate and the cathode product to be sodamide, presumably owing to a competitive reaction:-

$$Na_2O + 2NH_3 \rightarrow 2NaNH_2 + H_2O.$$

Other products such as sodium hyponitrite may also be formed.[68]

Sodium nitrate is remarkable in forming very few known double salts. Of these, darapskite, $Na_2SO_4,NaNO_3,H_2O$, is a constituent of Chilean *caliche* and since it appears as a wasteful by-product in the extraction of sodium nitrate considerable attention has been paid to its formation and properties. The sodium nitrate–sodium sulphate–water system has been described in detail by several authors:[69–73] the double salt is stable over the approximate temperature range 13° to 74°C. Its formation and decline over this temperature range in the presence of sodium chloride are illustrated in Figs. 2, 3, 4 and 5.[73] Above 74° the double salt dissociates and below 13° it appears to acquire a

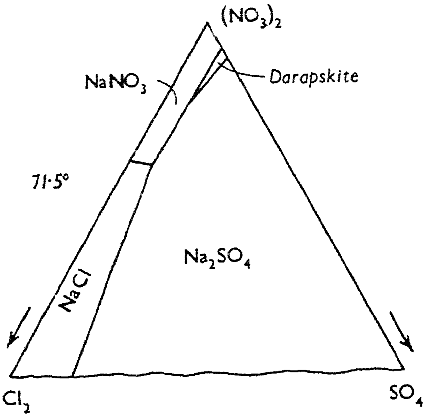

(NO$_3$)$_2$
NaNO$_3$
Darapskite
71·5°
Na$_2$SO$_4$
NaCl
Cl$_2$
SO$_4$

FIG. 2. SYSTEM NaNO$_3$-NaCl-Na$_2$SO$_4$-H$_2$O AT 71·5°C.

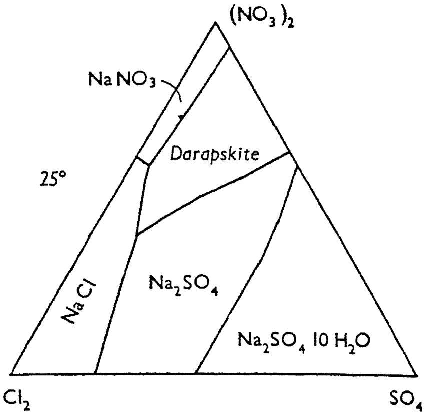

(NO$_3$)$_2$
Na NO$_3$
Darapskite
25°
Na$_2$SO$_4$
NaCl
Na$_2$SO$_4$ 10 H$_2$O
Cl$_2$
SO$_4$

FIG. 3. SYSTEM NaNO$_3$-NaCl-Na$_2$SO$_4$-H$_2$O AT 25°C.

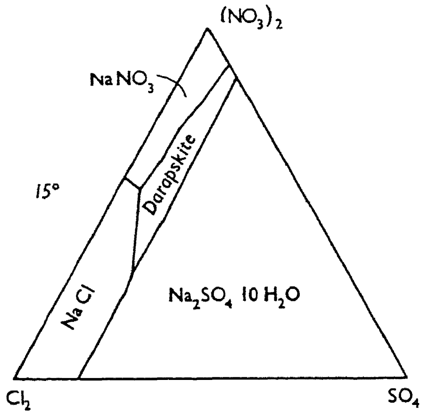

(NO$_3$)$_2$
NaNO$_3$
Darapskite
15°
NaCl
Na$_2$SO$_4$ 10 H$_2$O
Cl$_2$
SO$_4$

FIG. 4. SYSTEM NaNO$_3$-NaCl-Na$_2$SO$_4$-H$_2$O AT 15°C.

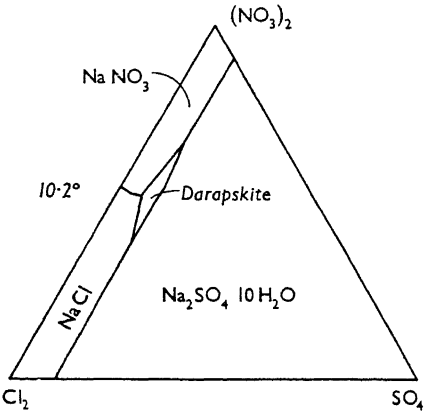

(NO$_3$)$_2$
Na NO$_3$
10·2°
Darapskite
NaCl
Na$_2$SO$_4$ 10 H$_2$O
Cl$_2$
SO$_4$

FIG. 5. SYSTEM NaNO$_3$-NaCl-Na$_2$SO$_4$-H$_2$O AT 10·2°C.

further nine molecules of water; in fact, the transition at 13·154 ± 0·0011°C. between the deca- and nona-hydrates is suggested as a fixed point in thermometry.[74] Darapskite also appears in the system Na_2SO_4-$NaNO_3$-K_2SO_4-H_2O at 50°.[75]

The prevention of formation of darapskite has also been studied and, in particular, the system $NaNO_3$-Na_2SO_4-$MgSO_4$-$Mg(NO_3)_2$-H_2O has received a good deal of attention.[69,76-81] From these investigations it is shown that the mineral double salt astrakanite, $MgSO_4$,Na_2SO_4,$4H_2O$, is much more stable than darapskite, and the formation of this 'protective agent' is favoured by adding appropriate quantities of a 'stabilizing agent' such as magnesium nitrate. Under such conditions, a solution of sodium nitrate containing sodium sulphate, magnesium salts, etc., deposits pure sodium nitrate on cooling. These relationships are illustrated in Figs. 6,[69] 7, 8 and 9[79] where it is clear that much

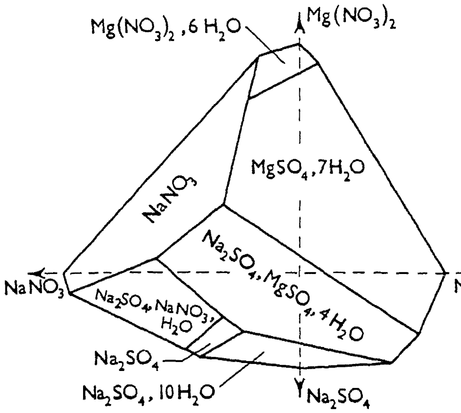

$Mg(NO_3)_2,6H_2O$
$Mg(NO_3)_2$
$NaNO_3$
$MgSO_4,7H_2O$
$Na_2SO_4,MgSO_4,4H_2O$
$NaNO_3$
$MgSO_4$
$Na_2SO_4,NaNO_3,H_2O$
Na_2SO_4
$Na_2SO_4,10H_2O$
Na_2SO_4

FIG. 6. SYSTEM $NaNO_3$-Na_2SO_4-$MgSO_4$-$MG(NO_3)_2$-H_2O AT 25°C.

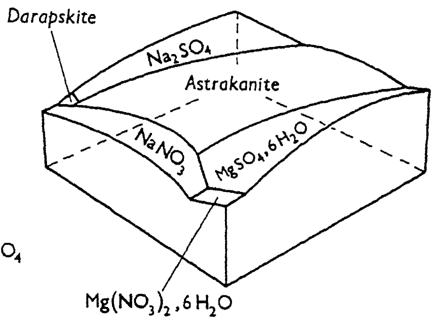
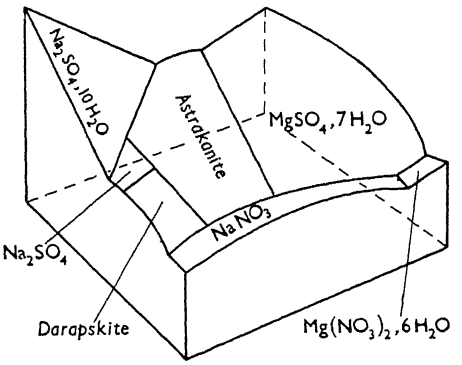

Darapskite
Na_2SO_4
Astrakanite
$NaNO_3$
$MgSO_4,6H_2O$
$Mg(NO_3)_2,6H_2O$

FIG. 7. SYSTEM $NaNO_3$-Na_2SO_4-$Mg(NO_3)_2$-$MgSO_4$-H_2O AT 50°C.


$Na_2SO_4,10H_2O$
Astrakanite
$MgSO_4,7H_2O$
$NaNO_3$
Na_2SO_4
Darapskite
$Mg(NO_3)_2,6H_2O$

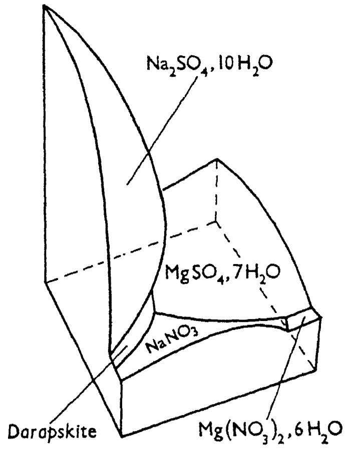

$Na_2SO_4,10H_2O$
$MgSO_4,7H_2O$
$NaNO_3$
Darapskite
$Mg(NO_3)_2,6H_2O$

FIG. 8. SYSTEM $NaNO_3$-Na_2SO_4-$Mg(NO_3)_2$-$MgSO_4$-H_2O AT 25°C.

FIG. 9. SYSTEM $NaNO_3$-Na_2SO_4-$Mg(NO_3)_2$-$MgSO_4$-H_2O AT 15°C.

of the area in the isotherms due to darapskite disappears in the presence of magnesium salts.

The density of the darapskite is given as 2·197 and the observed molecular volume as 111·6.[82]

The system NH_4NO_3-$NaNO_3$-H_2O at 25°, hitherto found to present only transition points, has been re-examined and the existence of a double compound, $2NaNO_3,NH_4NO_3$, possessing tetragonal syngony with an exothermic effect at 285° to 320° has been confirmed.[83,84] Other references to this system which do not mention double salt formation are given later. Similarly, most references to the system $NaNO_3$-$Ba(NO_3)_2$ make no reference to double salt formation, but freezing-point diagrams have suggested that a double salt $2Ba(NO_3)_2,NaNO_3$ does exist[85] though more recent investigation shows only the presence of eutectic mixtures.[86]

In the presence of aqueous sodium iodate, sodium nitrate forms a double salt $2NaIO_3,3NaNO_3,15H_2O$ up to approximately 10°. This forms a ternary eutectic at -11·49°, with ice, $NaIO_3,5H_2O$ and the double salt as the solid phases.[87-89] These relationships are illustrated in Figs. 10[88] and 11.[89]

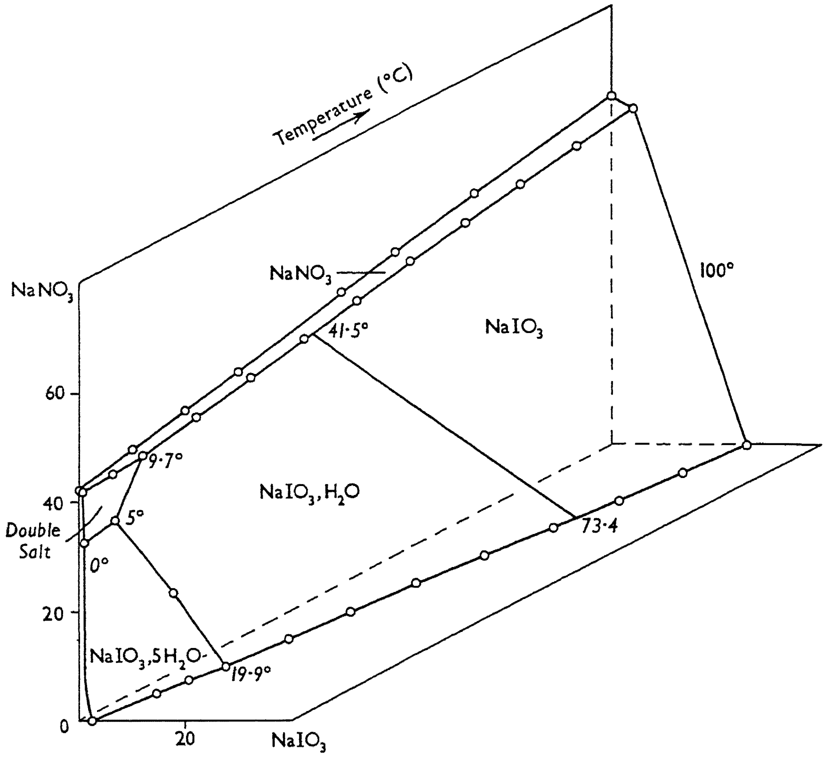


FIG. 10. ISOTHERMS OF THE TERNARY SYSTEM $NaIO_3$-$NaNO_3$-H_2O FROM 0 TO 100°C.

Polarographic methods have been employed in an attempt to investigate complex formation in the copper nitrate-sodium nitrate-water system.[90]

Measurement of interfacial tension between butyl acetate and aqueous solutions of sodium and lead nitrates leads to the conclusion that, in solution, the complex salts $4NaNO_3,Pb(NO_3)_2$, $2NaNO_3,Pb(NO_3)_2$ and $NaNO_3,Pb(NO_3)_2$ exist.[91,92] The following double salts with thorium nitrate, with their diamagnetic susceptibilities, have been reported.[93]

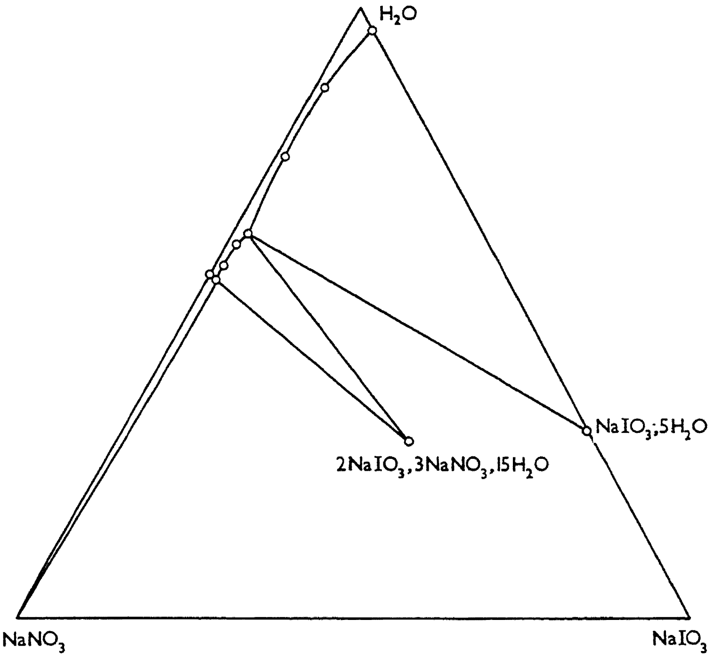


FIG. 11. 5° ISOTHERM FOR THE TERNARY SYSTEM $NaIO_3$-$NaNO_3$-H_2O

Salt	$\chi \times 10^6$	$\chi_M \times 10^6$ (calc.)	$\chi_M \times 10^6$ (obs.)
$NaNO_3$	-0·31	(-25·6[94])	-26·3
$2Th(NO_3)_4,NaNO_3,20H_2O$	-0·382	-	-547
$2Th(NO_3)_4,NaNO_3,8H_2O$	-0·282	-378	-335·6
$Th(NO_3)_4,NaNO_3,7H_2O$	-0·358	-244·7	-247·5
$Th(NO_3)_4,NaNO_3,2H_2O$	-0·237	-173·7	-118·8

A double compound, $NaSO_3NH_2,NaNO_3$, m.p. 205·7°, between sodium sulphamate and nitrate has been prepared;[95] it forms a eutectic mixture with 28·5% of sodium sulphamate in the melt at 199° and with 43·4% of sodium nitrate in the melt at 205°. Double 1:1 compounds with sodium butyrate and valerate, but not with formate, acetate, propionate, *iso*valerate or *iso*butyrate, are recognized by polythermal analysis.[37]

Cooling curves of mixtures of sodium nitrate and sodium hydroxide show that the two compounds $2NaOH,NaNO_3$ and $NaOH,NaNO_3$[96] are formed from the melt (see Fig. 12), but they cannot be prepared from solution; the melting points of these compounds have been given as 272° and 271·5°C.,[97] respectively, and it has been suggested that they be written in the ortho nitrate form as Na_3NO_4,H_2O and Na_2HNO_4.[97-100] The normal salt can be prepared by the violent action of heating sodium nitrate with sodium at 250° or by the relatively slow action of sodium peroxide on sodium nitrite at 300° to 350°C.[99] Water readily decomposes the orthonitrates into nitrite and sodium oxide, and the last compound appears to be very loosely combined, so much so that the

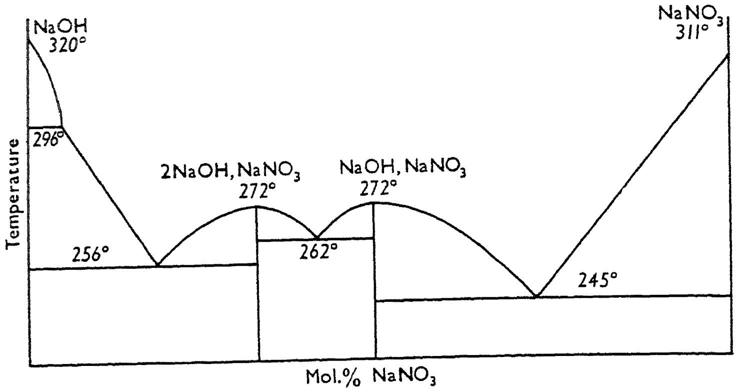


FIG. 12. THE BINARY SYSTEM NaOH-$NaNO_3$

orthonitrate ion does not appear to be an independent group in the crystal lattice.[99] Action of excess sodium oxide at 300° under vacuum on the orthonitrate gives sodium nitrite.[101]

The systems given in Table XXV are those that do *not* yield double salts under the conditions described. Notes are appended on points of interest in the systems investigated.

TABLE XXV. - SYSTEMS INVOLVING SODIUM NITRATE, WHICH DO *NOT* CONTAIN DOUBLE COMPOUNDS OF SODIUM NITRATE

Components of the system with $NaNO_3$	Notes	Reference
HNO_3-H_2O	1. Solubility of $NaNO_3$ reduced by HNO_3	102
	2. Ionic equilibria of HNO_3 unaffected by addition of $NaNO_3$	103
	3. Divided into 2 systems by a fold due to $NaNO_3$	104
HNO_3-H_2Cl_2-H_2O	1. Equilibrium is displaced towards HNO_3 in solutions of high acidity, so that $NaNO_3$ can be separated	105
	2. Solubility ratio $NaNO_3$:NaCl increases with temperature and acidity. Eutonic point at 15° lies on line NaCl-H_2O in tetrahedral model	106
	3. Eutonic point is within tetrahedral model at point of minimum vapour pressure and maximum salt content	107
HNO_3-$Al(NO_3)_3$-H_2O	No mixed crystal formation	108
NH_4NO_3	1. Cooling curves show eutectic at 121·2° and transition point at 126·2° containing 21·0 and 18·0% of $NaNO_3$ respectively	109
	2. Eutectic at 121·1° containing: NH_4NO_3, 78·2%; $NaNO_3$, 21·8%. For γ-NH_4NO_3-$NaNO_3$ a metastable eutectic at 117·0° is predicted	110

continued on following page

TABLE XXV (continued)

Components of the system with $NaNO_3$	Notes	Reference
NH_4NO_3–H_2O	1. Eutectic at −25·7° containing: $NaNO_3$, 25·7%; NH_4NO_3, 25·4%; H_2O, 48·9%	111
	2.	112
NH_4NO_3–NH_4Cl–$NaCl$	Ternary points: 112° (NH_4NO_3 + NH_4Cl + $NaNO_3$) and 133° ($NaCl$ + NH_4Cl + $NaNO_3$). No double salts or isomorphous mixtures are formed	113
NH_4NO_3–KNO_3	1. Eutectic, f.p. 118·5°, containing: NH_4NO_3, 66·5%; $NaNO_3$, 21·0%; KNO_3, 12·5%	114
	2. Mixed KNO_3–NH_4NO_3 crystals separate. A eutectic is formed from 3 invariant ternary points at 119°, 128° and 153°	115
NH_4NO_3–$AgNO_3$	Eutectics at 95° containing: NH_4NO_3, 55·5%; $AgNO_3$, 36·5%; $NaNO_3$, 8·0%; and 94°: NH_4NO_3, 67·5%; $AgNO_3$, 20·5%; $NaNO_3$, 12·0%	116
NH_4NO_3–$Ca(NO_3)_2$	Eutectic, f.p. 107·5° containing: NH_4NO_3, 69%; $Ca(NO_3)_2$, 18%; $NaNO_3$, 13(?)%	114
NH_4NO_3–$Pb(NO_3)_2$–H_2O	Eutectic at 112·3° containing: δ-NH_4NO_3, 75·9 mol.%; $NaNO_3$, 17·8 mol.%; $Pb(NO_3)_2$, 6·3 mol.%. For γ-NH_4NO_3-$NaNO_3$-$Pb(NO_3)_2$ a metastable eutectic is predicted at 109·4°	117
NH_4NO_3–$CO(NH_2)_2$	Eutectic, f.p. 37·1° containing: NH_4NO_3, 47·5%; urea, 45·0%; $NaNO_3$, 7·5%	118
$NH_4H_2PO_4$–H_2O	1. Eutectic at −20·6° containing as the solid phases: ice, 58·7%; $NaH_2PO_4 . 2H_2O$, 33·3%; $NaNO_3$, 8·0%	119
	2.	111
$LiNO_3$	Conductivity measurements from 180° to 270°	120
$LiNO_3$–$Cd(NO_3)_2$	Invariant point at m.p. 110° containing: $Cd(NO_3)_2$, 56·0 mol.%; $NaNO_3$, 29·5 mol.%; $LiNO_3$, 14·5 mol.%	121
$NaNO_2$–H_2O	1. Isotherm at 15°	122
	2.	123
Na_2HPO_4–H_2O	1. Eutectic at −19·4° containing, as the solid phases; ice, 61·8%; $NaNO_3$, 30·8%; NaH_2PO_4, 7·4%	124
	2.	119

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TABLE XXV (continued)

<table>
<tr><th>Components of the system with $NaNO_3$</th><th>Notes</th><th>Reference</th></tr>
<tr><td>$NaOH-LiNO_3-LiOH$</td><td>Irreversibly reciprocal</td><td>125</td></tr>
<tr><td>$NaOH-KNO_3-KOH$</td><td></td><td>49</td></tr>
<tr><td>$NaOH-RbNO_3-RbOH$</td><td></td><td>49</td></tr>
<tr><td>$NaOH-CsNO_3-CsOH$</td><td></td><td>49</td></tr>
<tr><td>$Na_2SO_4-Na_2CrO_4$</td><td>1.</td><td>126</td></tr>
<tr><td></td><td>2.</td><td>127</td></tr>
<tr><td>$Na_2SO_4-KNO_3-K_2SO_4$</td><td></td><td>128</td></tr>
<tr><td>$Na_2CrO_4-H_2O$</td><td></td><td>129</td></tr>
<tr><td>$Na_2CrO_4-KNO_3-K_2CrO_4$</td><td></td><td>130</td></tr>
<tr><td>$Na_2Cr_2O_7$</td><td>Eutectic at 262° containing: $NaNO_3$, 54·6%; $Na_2Cr_2O_7$, 45·4%</td><td>131</td></tr>
<tr><td>$Na_2Cr_2O_7-KNO_3$</td><td>Eutectics at 215° containing: KNO_3, 61·2%; $Na_2Cr_2O_7$, 23·5%; $NaNO_3$, 15·3%: at 225° containing: $Na_2Cr_2O_7$, 48·8%; KNO_3, 41·0%; $NaNO_3$, 10·2%: and at 253° containing: $NaNO_3$, 44·9%; $Na_2Cr_2O_7$, 43·5%; KNO_3, 11·6%</td><td>131</td></tr>
<tr><td>$Na_2MoO_4-H_2O$</td><td>No solid solutions at 25°</td><td>132</td></tr>
<tr><td>NaF</td><td>Eutectic at 304° containing: $NaNO_3$, 96·5 mol.%; NaF, 3·5 mol.%</td><td>51</td></tr>
<tr><td>$NaF-KNO_3$</td><td>Minimum at 228°</td><td>51</td></tr>
<tr><td>$NaF-KNO_3-KF$</td><td>Singular irreversibly reciprocal system</td><td>51</td></tr>
<tr><td>$NaCl$</td><td></td><td>133</td></tr>
<tr><td>$NaCl-KNO_3-KCl$</td><td></td><td>50</td></tr>
<tr><td>$NaCl-KNO_3-KCl-Mg(NO_3)_2-MgCl_2$</td><td></td><td>134</td></tr>
<tr><td>$NaCl-Ba(NO_3)_2-BaCl_2-H_2O$</td><td></td><td>135</td></tr>
<tr><td>$NaBr-KNO_3-KBr$</td><td>Reversible reciprocal system</td><td>50</td></tr>
<tr><td>$NaI-KNO_3-KI$</td><td></td><td>50</td></tr>
<tr><td>$NaI-AgNO_3-AgI$</td><td>Eutectics are as follows (mol.%):
<table>
<tr><th>Temp. (°C.)</th><th>$AgNO_3$</th><th>AgI</th><th>NaI</th><th>$NaNO_3$</th></tr>
<tr><td>110</td><td>73·0</td><td>26·0</td><td>0</td><td>1·0</td></tr>
<tr><td>102</td><td>55·0</td><td>43·5</td><td>0</td><td>1·5</td></tr>
<tr><td>98</td><td>40·25</td><td>59·0</td><td>0</td><td>0·75</td></tr>
<tr><td>286</td><td>0</td><td>0·5</td><td>14·0</td><td>85·5</td></tr>
</table></td><td>52</td></tr>
<tr><td>KNO_3</td><td>1. Minimum in cooling curves at 225·7°, corresponding to: KNO_3, 55%; $NaNO_3$, 45%</td><td>136</td></tr>
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<tr><td></td><td>2. Eutectic solubilities at 0°, 20°, 40°, 60°</td><td>142</td></tr>
</table>

continued on following page

TABLE XXV (continued)

Components of the system with $NaNO_3$	Notes	Reference
	3. Eutectic at $-19{\cdot}0^{\circ}$ containing: H_2O, 57·54%; $NaNO_3$, 36·88%; KNO_3, 5·58%	137
KNO_3–$K_2Cr_2O_7$	Eutectic at 216° containing: $NaNO_3$, 47·1%; KNO_3, 37·0%; $K_2Cr_2O_7$, 15·9%: and at 216°: $NaNO_3$, 52·9%; $K_2Cr_2O_7$, 24·5%; KNO_3, 22·7%	131
KNO_3–$AgNO_3$		143
KNO_3–$AgNO_3$–$TlNO_3$	Eutectic at 76° containing: $AgNO_3$, 52·0 mol.%; $TlNO_3$, 45·8 mol.%; $NaNO_3$, 1·7 mol.%; KNO_3, 0·5 mol.%. Transition points at 85° and 94°, and a transformation point at 107°	143
KNO_3–$TlNO_3$		143
KNO_3–$Mg(NO_3)_2$		144
KNO_3–$Mg(NO_3)_2$–$Ca(NO_3)_2$		144
KNO_3–$Ca(NO_3)_2$	1.	144
	2. Eutectic at 133°	145
	3. Eutectic at 133°. Ternary transition point at 160° containing: KNO_3, 53·9%; $Ca(NO_3)_2$, 29·4%; $NaNO_3$, 16·7%	146
	4. Eutectic at 133° containing: $Ca(NO_3)_2$, 48·8%; KNO_3, 39·4%; $NaNO_3$, 11·8%. Ternary transition point at 160° containing: KNO_3, 49·2%; $Ca(NO_3)_2$, 32·8%; $NaNO_3$, 18·0%	139
KNO_3–$Ca(NO_3)_2$–H_2O	No mixed crystal formation at 0° and 20°	147
KNO_3–$Sr(NO_3)_2$	Minimum at 208° containing: $NaNO_3$, 45·0 mol.%; KNO_3, 44·7 mol.%; $Sr(NO_3)_2$, 10·3 mol.%	7
KNO_3–$Ba(NO_3)_2$	No ternary eutectic, but a minimum at 216° containing: $(KNO_3)_2$, 48·6 mol.%; $(NaNO_3)_2$, 46·0 mol.%; $Ba(NO_3)_2$, 5·4 mol.%	86
KNO_3–$Al(NO_3)_3$–H_2O	No mixed crystal formation from 0° to 60°	142
KNO_3–$Pb(NO_3)_2$	Ternary mixture with minimum f.p. has the composition: KNO_3, 44%; $Pb(NO_3)_2$, 33%; $NaNO_3$, 23%. F.p. $185{\cdot}6^{\circ}$	148
$KClO_4$–H_2O		149
$RbNO_3$	Eutectic at $178{\cdot}5^{\circ}$ containing: $RbNO_3$, 55 mol.%; $NaNO_3$, 45 mol.%	150
$AgNO_3$	1.	143

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TABLE XXV (continued)

Components of the system with $NaNO_3$	Notes	Reference
	2.	151
$AgNO_3$-$TlNO_3$	Eutectic at 78° containing: $AgNO_3$, 51·8 mol.%; $TlNO_3$, 46·0 mol.%; $NaNO_3$, 2·2 mol.%: and at 79° containing: $TlNO_3$, 51·3 mol.%; $AgNO_3$, 46·4 mol.%; $NaNO_3$, 2·3 mol.%	143
$AgNO_3$-$Ba(NO_3)_2$	Eutectic containing: $AgNO_3$, 65·745%; $NaNO_3$, 31·655%; $Ba(NO_3)_2$, 2·670%	152
$Mg(NO_3)_2$		144
$Mg(NO_3)_2$-H_2O	No solid solutions are formed	153
$Mg(NO_3)_2$-$Ca(NO_3)_2$		144
$CaCO_3$-H_2O	No mixed crystal formation	154
$Ca(NO_3)_2$	1.	144
	2.	147
	3. Simple eutectic at 232° containing: $NaNO_3$, 54·1%; $Ca(NO_3)_2$, 45·9%	146
	4. Eutectic at 232° containing: $NaNO_3$, 54·1%; $Ca(NO_3)_2$, 45·9%	139
	5.	155
$Ca(NO_3)_2$-$Ba(NO_3)_2$		155
$Ca(NO_3)_2$-$Ra(NO_3)_2$	1.	156
	2.	157
$Sr(NO_3)_2$	1.	155
	2.	158
	3. Eutectic at 287° containing: $NaNO_3$, 90·5 mol.%; $Sr(NO_3)_2$, 9·5 mol.%	7
$Sr(NO_3)_2$-$Ba(NO_3)_2$		155
$Sr(NO_3)_2$-$Pb(NO_3)_2$		155
$Ba(NO_3)_2$	1.	86
	2.	155
$Ba(NO_3)_2$-$Ra(NO_3)_2$		159
$Ba(NO_3)_2$-$Pb(NO_3)_2$		155
$Cd(NO_3)_2$	1. Eutectic, m.p. 135°, containing: $Cd(NO_3)_2$, 64·0 mol.%; $NaNO_3$, 36·0 mol.%	121
	2.	160
$Al(NO_3)_3$-H_2O	No mixed crystal formation from 0° to 60°	142
$Pb(NO_3)_2$	Eutectics are formed	161
$Pb(NO_3)_2$-H_2O	1.	162
	2.	163
	3. Faraday rotation phenomena exclude double compound formation	164
	4. Eutonic solution containing: $NaNO_3$, 42·0%; H_2O, 41·2%; $Pb(NO_3)_2$, 16·8%	165

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SECTION XXXVIII

SODIUM PHOSPHATE

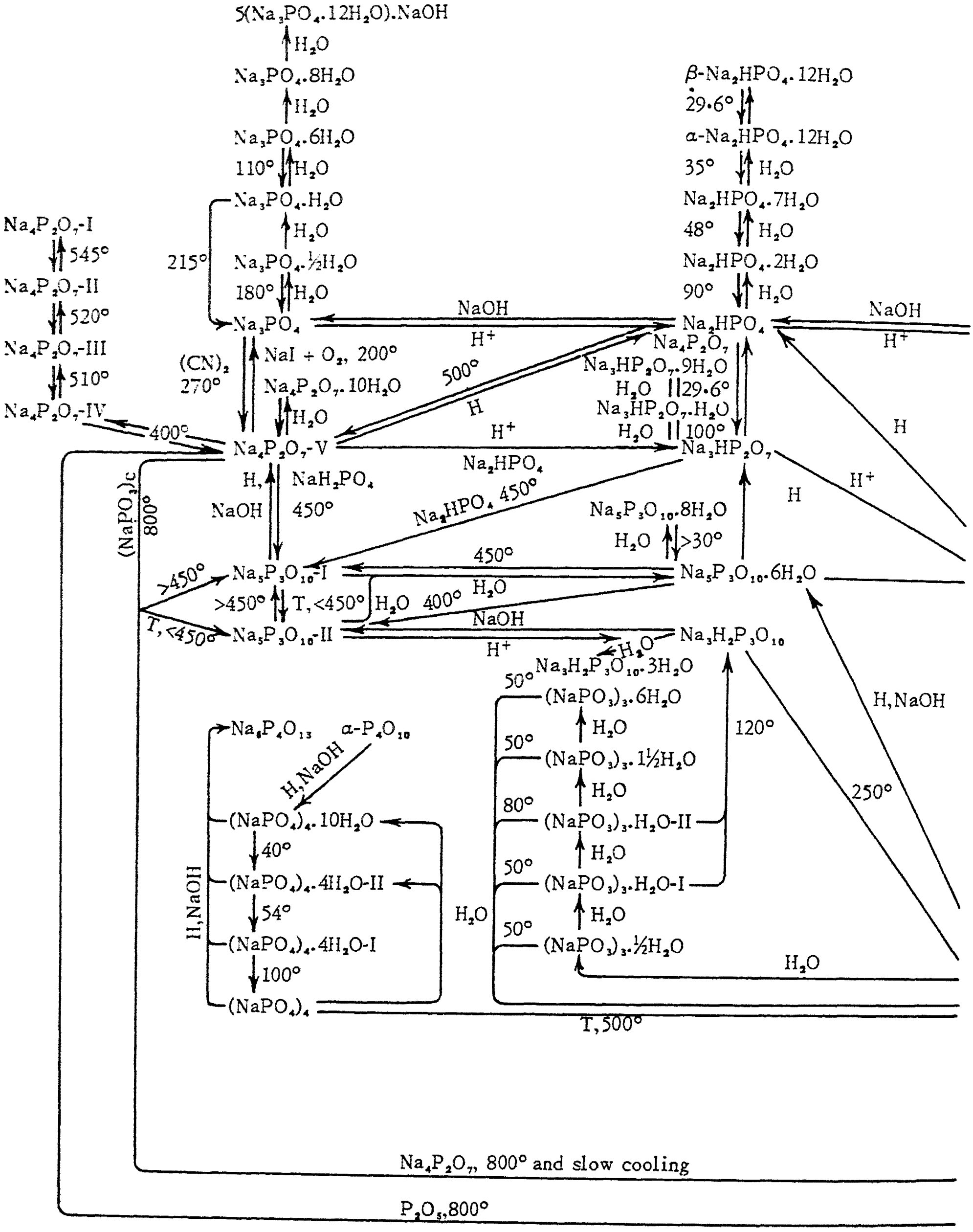
By D. A. PANTONY

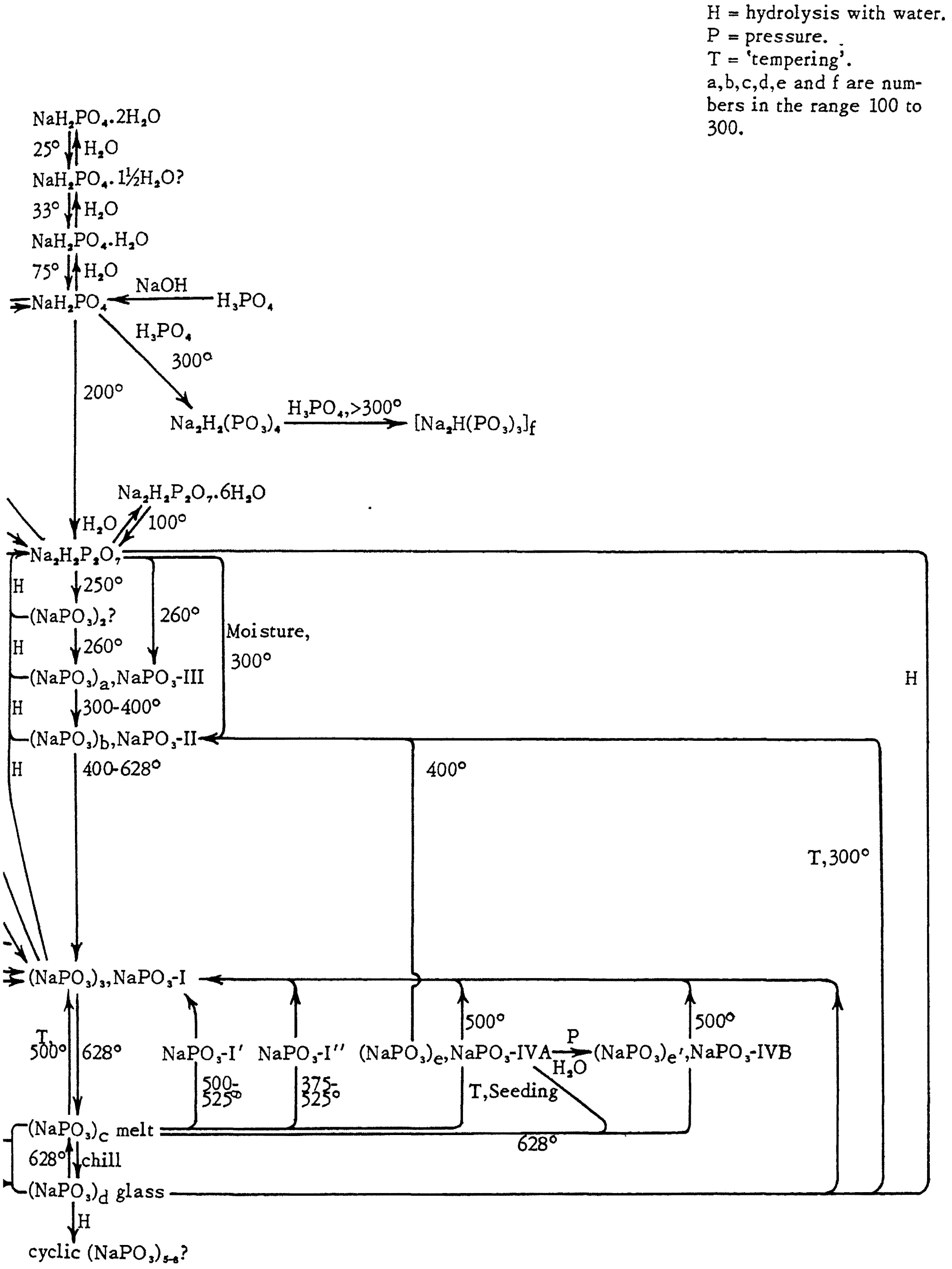
GENERAL INTRODUCTION

The chemistry of 'sodium phosphate' covers the chemistry of at least fifty different species of compound. These are largely interconvertible and a slightly simplified general outline of their relationships is given in the scheme. (see pages 1260 and 1261) Of special interest is the discovery of the several forms of the compound of empirical formula $NaPO_3$, the metaphosphates. In this field, and in that of the polyphosphates, the past thirty years has seen a tremendous advance in the utilization of these compounds and in the understanding of their chemistry. Several reviews of considerable value relating to sodium phosphate preparation,[1-11] uses,[4,6-9,12-21] and properties[4-8,20,22-31] and certain critical surveys or repetitions of earlier work[5,23,24,26-30,32-40] have been published.

As one consequence of the increased interest in sodium phosphate chemistry there appear, especially in patent literature, many references to the preparation and uses of the sodium phosphates. Although this literature is extensive, individual papers contribute but little new to the chemistry of this field. Again, in considering the chemical and physical properties the position is often obscured because the results of several schools of workers are often conflicting and care must be exercised in accepting unsubstantiated statements.

No work has been reported on naturally occurring mineral sodium phosphates, although new crystallographic data on some sodium-iron and sodium-manganese phosphates have been published.[41]


$5(Na_3PO_4.12H_2O).NaOH$
H_2O
$Na_3PO_4.8H_2O$
H_2O
$Na_3PO_4.6H_2O$
110°
H_2O
$Na_3PO_4.H_2O$
H_2O
215°
$Na_3PO_4.\frac{1}{2}H_2O$
180°
H_2O
Na_3PO_4
$Na_4P_2O_7$-I
545°
$Na_4P_2O_7$-II
520°
$Na_4P_2O_7$-III
510°
$Na_4P_2O_7$-IV
400°
$(CN)_2$
270°
$NaI + O_2$, 200°
$Na_4P_2O_7.10H_2O$
H_2O
$Na_4P_2O_7$-V
β-$Na_2HPO_4.12H_2O$
29·6°
α-$Na_2HPO_4.12H_2O$
35°
H_2O
$Na_2HPO_4.7H_2O$
48°
H_2O
$Na_2HPO_4.2H_2O$
90°
H_2O
NaOH
H^+
Na_2HPO_4
NaOH
H^+
500°
H
$Na_4P_2O_7$
$Na_3HP_2O_7.9H_2O$
H_2O
29·6°
$Na_3HP_2O_7.H_2O$
H_2O
100°
H^+
$Na_3HP_2O_7$
H
H^+
H
Na_2HPO_4
$(NaPO_3)c$
800°
H
NaOH
NaH_2PO_4
450°
Na_2HPO_4 450°
$Na_5P_3O_{10}.8H_2O$
H_2O
>30°
450°
$Na_5P_3O_{10}$-I
$Na_5P_3O_{10}.6H_2O$
>450°
>450°
T, <450°
H_2O
400°
H_2O
NaOH
T, <450°
$Na_5P_3O_{10}$-II
H^+
H_2O
$Na_3H_2P_3O_{10}$
$Na_3H_2P_3O_{10}.3H_2O$
50°
$(NaPO_3)_3.6H_2O$
H_2O
50°
$(NaPO_3)_3.1\frac{1}{2}H_2O$
H_2O
80°
$(NaPO_3)_3.H_2O$-II
H_2O
50°
$(NaPO_3)_3.H_2O$-I
H_2O
50°
$(NaPO_3)_3.\frac{1}{2}H_2O$
120°
H,NaOH
250°
H_2O
$Na_6P_4O_{13}$
α-P_4O_{10}
H,NaOH
$(NaPO_4)_4.10H_2O$
40°
$(NaPO_4)_4.4H_2O$-II
54°
$(NaPO_4)_4.4H_2O$-I
100°
$(NaPO_4)_4$
H,NaOH
H_2O
T,500°
$Na_4P_2O_7$, 800° and slow cooling
P_2O_5,800°



H = hydrolysis with water.
P = pressure.
T = 'tempering'.
a,b,c,d,e and f are numbers in the range 100 to 300.

$NaH_2PO_4.2H_2O$
25°
H_2O
$NaH_2PO_4.1\frac{1}{2}H_2O$?
33°
H_2O
$NaH_2PO_4.H_2O$
75°
H_2O
NaOH
NaH_2PO_4
H_3PO_4
H_3PO_4
300°
200°
$Na_2H_2(PO_3)_4$
H_3PO_4,>300°
$[Na_2H(PO_3)_3]_f$
$Na_2H_2P_2O_7.6H_2O$
H_2O
100°
$Na_2H_2P_2O_7$
H
250°
$(NaPO_3)_2$?
260°
H
260°
Moisture, 300°
$(NaPO_3)_a,NaPO_3$-III
H
300-400°
$(NaPO_3)_b,NaPO_3$-II
H
400-628°
400°
H
T,300°
$(NaPO_3)_3,NaPO_3$-I
T, 500°
628°
$NaPO_3$-I'
$NaPO_3$-I''
$(NaPO_3)_e,NaPO_3$-IVA
P
H_2O
$(NaPO_3)_{e'},NaPO_3$-IVB
500°
500°
500-525°
375-525°
T,Seeding
628°
$(NaPO_3)_c$ melt
628°
chill
$(NaPO_3)_d$ glass
H
cyclic $(NaPO_3)_{5-6}$?

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SODIUM ORTHOPHOSPHATES

Trisodium Orthophosphate

Preparation.

Mineral or rock phosphates, such as calcium, aluminium or iron phosphatic minerals or monazite or bone ash, are sources of trisodium phosphate, known in commerce as 'TSP'. The mineral is treated either with alkaline sodium compounds such as sodium hydroxide,[1-11] sodium carbonate,[12,13] sodium silicate[14,15] or sodium aluminate[16] in aqueous solution, or alternatively with sulphuric acid (sometimes with added phosphoric acid to obtain the correct phosphate balance) followed by a sodium salt or base such as sodium carbonate[17-22] at high temperature (200° to 500°C.) and sometimes under pressure. Other methods, using less active reagents but usually more extreme physical conditions, involve the extraction of the minerals with superheated water in the presence of a sodium salt[23-25] such as sodium nitrate or chloride.[26] It is said that calcium phosphate may be extracted with sodium sulphate solution in the presence of sulphur dioxide[27] or with sodium fluoride[28,29] with subsequent recovery of sodium phosphate.

Sodium phosphate may also be prepared by calcining or sintering (but not melting) mineral phosphates with a sodium salt[30-36] usually in the presence of carbon; the desired product is readily extracted from the cooled cake with water. A third type of process which has received considerable attention is based on the reaction of metal phosphides, especially 'ferrophosphorus', with sodium sulphate (added as such or produced from ferrous sulphide or pyrites in the presence of a sodium salt and air[37-39]) or with sodium carbonate, or sodium nitrate, sulphate, sulphite or chloride sometimes in the presence of carbonate and carbon at a high temperature.[40-57] The presence or absence of oxygen does not appear to affect the reaction unless sulphides are employed. Ferrophosphorus may be extracted in an autoclave with aqueous sodium carbonate or hydroxide,[58] or it may be fused with pyrites and the cake extracted with hydrochloric acid, the resulting solution of phosphoric acid being treated with sodium hydroxide.[59]

Several references have been made to the preparation of trisodium orthophosphate from solutions of the acid sodium orthophosphates, particularly disodium hydrogen phosphate, and from phosphoric acid by the action of sodium hydroxide[60-62] or carbonate[63-65] or both,[66-68] or by using sodium carbonate or chloride in the presence of aqueous ammonia.[69,70] Solid hydrated disodium hydrogen phosphate when ground intimately with sodium hydroxide is said to yield the normal salt[71] and at high temperatures (above 200°C.) other sodium salts can be employed to convert the acid phosphates to trisodium phosphate.[72-79] The action of sodium pyrophosphate on sodium iodide in the presence of oxygen is stated to yield trisodium orthophosphate:-[80]

$$2NaI + Na_4P_2O_7 + \tfrac{1}{2}O_2 \rightarrow 2Na_3PO_4 + I_2$$

Reference has also been made to the recovery of trisodium phosphate by hydrolysis of condensed phosphates[81-84] with water or sodium hydroxide and by electrolysis of disodium hydrogen phosphate in a diaphragm cell.[85]

The solutions of trisodium phosphate obtained in any of the commercial processes are treated with barium carbonate to remove sulphate, with sodium sulphide to remove arsenic or lead, or with barium sulphide to remove both classes of impurities[86,87] and are crystallized to give the 'dodecahydrate', usually referred to as $Na_3PO_4,12H_2O$, which invariably contains a slight excess (approximately 2%) of sodium hydroxide. Large excesses of sodium hydroxide lead to complex salts such as $9(Na_3PO_4,12H_2O),2NaOH$.[88] For convenience of transportation and use, the 'dodecahydrate' is usually heat-treated to produce a substance approximating to the nona- or deca-hydrate.

A double salt, $2Na_3PO_4,NaF,19H_2O$, is reported to be formed when phosphate minerals containing fluorine are roasted with sodium carbonate or heated with aqueous sodium hydroxide under pressure[89] and, although much of the fluoride precipitates as its sodium salt during the commercial preparation of sodium phosphates, undoubtedly some must remain in the final product derived from almost any natural phosphate.[90]

Uses.

Trisodium orthophosphate has found use as a constituent of cleaning solutions and powders[91-111] and for softening water and preventing scale formation in boilers.[112-119] In the food industry the salt has been used for cleaning equipment, for improving the texture of cheese,[120] for deliming sugar liquors,[121-123] and for improvement of fruit juice storage[124] and extraction,[125] but care must be exercised owing to its corrosive action on certain items of equipment;[126,127]

against which, however, sodium chromate is said to be an effective protective agent.[128] The phosphate has been used as an additive to sodium hydroxide in the refining of glycoside fats[129] and as a fungicide in several compositions[90,130-132] but not as an algicide.[133] The use of TSP as a fertilizer has been examined;[134] it has also been used in diazotype copy developers[135] and in the treatment of paper before coating with resins.[136] The salt has been employed as a constituent of drilling muds,[137] and in the flotation of silica minerals,[138] and it has been shown to assist in the thermal decomposition of aluminous phosphate rocks.[139] A glue containing 100 parts of water glass and 5 parts of anhydrous trisodium phosphate has been recommended as an adhesive for bakelite, paper and porcelain;[140] certain fire-proof and water-proof coatings also contain the normal sodium phosphate.[141-142] Latex and polyvinyl chloride emulsions are stabilized by the salt.[143,144]

Trisodium phosphate is commonly used as a means of removing ferruginous and other cations[145,146] in purification processes. It has been used in the preparation of pure stable cupric hydroxide.[147] Efforts have been made to use the salt as a constituent of fusible enamels in place of borax[148,149] but complete replacement is not practicable owing to the attendant increase in the coefficient of thermal expansion. A recipe for a phosphatizing bath for metallic objects contains the salt.[150] It has been stated that trisodium phosphate inhibits pitting corrosion on metals especially by chloride solutions[151-154] (mainly owing to its alkalinity), by surface active agents[155,156] and by several other agents,[157-166] but it has been reported that latex film used as a protection against corrosion is attacked by solutions of the salt.[167]

Physical Properties.

The apparent density of powdered anhydrous trisodium phosphate is given as 1·09.[168] The space group is D_{3d}^4 with *a* 12·02 and *c* 12·66A.[169] (cf. the *a*:*c* ratio of 1:0·5324 given for the trigonal rhombohedral structure[170]). An examination of the infra-red spectrum of the anhydrous salt shows[171] very strong, broad absorption bands between 1125 and 1028 cm.$^{-1}$ and a very weak band at 914 cm.$^{-1}$ The Raman spectrum displays a $\Delta\nu_4$ frequency of 937 cm.$^{-1}$ when excited by the 4358A. mercury line: some shift occurs in solution.[172] The salt has been used as a target for deuteron bombardment, whereby α-particles and long-range protons are emitted.[173] A minimum value of 7·3 is given for the dielectric constant of the anhydrous powder,[174] and its variation over the range 83 to 293°K. at 9500Mc. has been investigated.[168]

The solubility of the normal salt in water has been given as 49·7% at 105°C., decreased by the addition of sodium chloride,[175] 61·1g./100g. of water at 83°C. and 0·15g./100g. of water at 350°C., decreased by the addition of sodium hydroxide, especially at low temperatures.[176] A 0·01M. solution of the salt at 25°C. has been recommended as a practical pH standard of 11·72 for the extreme end of the pH scale,[177] and the pH values of various concentrations of aqueous trisodium phosphate have been determined[178] (Table I). Conductivities for saturated solutions of the salt are shown in Table II;[179] this property shows a positive pressure coefficient.[180] Activity and osmotic coefficients at 25°C. are given in Table III, together with those of the other sodium orthophosphates.[181] The chemical potential of water in these solutions has also been examined experimentally.

Sound absorption in solutions of trisodium phosphate over the range 4×10^3 to 10^8 cycles/sec.[182] and at 3×10^8 cycles/sec.[183] has been examined; ultrasonic absorption shows a shift of relaxation frequency with concentration of the salt.[184] The surface tension of a 1% solution is given as 72·46 dynes/cm.[104] and a molar solution is said to increase markedly the interfacial tension between mercury and water.[185] The viscosity of aqueous solutions of the salt

TABLE I. - pH OF SOLUTIONS OF TRISODIUM PHOSPHATE

Concentration		pH
g./l.	meq./l.	
26·3	207·5	12·2
13·1	103·7	12·1
5·26	41·5	11·9
2·63	20·8	11·7
0·53	4·2	11·1
0·26	2·08	10·7

TABLE II. - SPECIFIC CONDUCTIVITY DATA FOR SATURATED SOLUTIONS OF TRISODIUM ORTHOPHOSPHATE[179]

Temperature (°C.)	Specific conductivity (mho cm.^{-3})
25·0	0·0702
30·0	0·0821
34·8	0·0867
42·8	0·0973
50·0	0·104
64·0	0·187
75·0	0·228

TABLE III. - OSMOTIC AND ACTIVITY COEFFICIENTS OF SOLUTIONS OF TRISODIUM ORTHOPHOSPHATE[181]

Molarity	Osmotic coefficients			Activity coefficients (1+log γ)		
	Na_3PO_4	Na_2HPO_4	NaH_2PO_4	Na_3PO_4	Na_2HPO_4	NaH_2PO_4
0·1	0·678	0·802	0·913	0·467	0·681	0·876
0·2	0·618	0·754	0·884	0·335	0·593	0·833
0·3	0·579	0·720	0·862	0·247	0·532	0·801
0·4	0·550	0·693	0·844	0·180	0·484	0·775
0·5	0·527	0·670	0·829	0·126	0·443	0·752
0·6	0·508	0·651	0·816	0·079	0·408	0·732
0·7	0·492	0·634	0·804	0·039	0·377	0·715
0·8	-	0·620	0·794	-	0·349	0·698
0·9	-	0·608	0·784	-	0·334	0·684
1·0	-	0·596	0·776	-	0·301	0·670
1·1	-	0·586	0·768	-	0·279	0·657
1·2	-	-	0·761	-	-	0·645
1·3	-	-	0·755	-	-	0·634

has been treated theoretically and calculated values compared with experimental values.[186]

The influence of trisodium phosphate on other systems has also been investigated, for example on the rate of oxidation of iodine to iodate;[187] and on the galvoluminescence of aluminium anodes.[188] The salt is said to stabilize the α-form of calcium silicate, $2CaO,SiO_2$, at high temperatures and impedes the $\beta \rightarrow \gamma$ transformation;[189] the behaviour of sodium phosphate on anion exchange resins has been studied;[190] solutions of the normal salt lower the 'critical' concentration for micelle formation in sodium laurate solutions[191] and micellar molecular weights of surface active agents are increased, then decreased and finally again increased in successively increasing concentrations of the salt.[192] It is said that TSP disperses laterite effectively but not other soils;[193] the adsorption of all the sodium orthophosphates on colloidal hydrated ferric oxide has been discussed;[194] dialysis of sodium and of orthophosphate ions in contact with cellulose ester membranes shows a preference for the cation which varies, possibly becoming negative, depending on the time of contact and on pH.[195] The viscosity of 55% aqueous sucrose solutions is markedly increased by trisodium phosphate between 20° and 60°C., an effect due mainly to the anion,[196] and similar effects have been reported for dilute polymer solutions.[197] Autolysis and autophagy of *Staphylococcus aureus* is promoted by solutions of the salt.[198]

Chemical Properties.

The hydration of trisodium phosphate has been the subject of much discussion. In an examination of the 'dodecahydrate' it has been suggested that slowly cooled supersaturated solutions may contain an unstable higher hydrate.[169] In the system Na_2O–P_2O_5–H_2O, the presence of stable dodeca-, hexa- and hemi-hydrates and, possibly, an octahydrate, depending on the sodium concentration and on temperature, has been recognized.[199] At 120–215°C. an aqueous solution is in equilibrium with a monohydrate and at 215–350°C. with the anhydrous salt.[176] The existence of the hexa- (m.p. 110°C.), hemi- (effloresces at 180°C.) and octa-hydrates has been confirmed and the salts isolated; all other higher hydrates in the solid state are complex salts containing a monobasic anion – e.g., $9(Na_3PO_4,12H_2O),2NaOH$[88] or $5Na_3PO_4,12H_2O),NaOH$, the 'trisodium orthophosphate dodecahydrate' which is the main constituent of TSP. This formula is an example of the isomorphous series $n(Na_3PO_4,xH_2O),NaY$, analogous to the vanadates, where n is 4 to 7, x is 11 or 12 and Y can be OH or NO_3.[200] This series is to be differentiated from the type nNa_3PO_4,NaY,xH_2O where n is 1 or 2, Y is a univalent anion and x is 18 or 19, exemplified by $Na_3PO_4,NaBO_2,18H_2O$[201] and $2Na_3PO_4,NaF,19H_2O$.[89] The sodium hypochlorite–trisodium phosphate substances that have found use in detergent compositions are prepared by direct interaction of the constituent salts[202,203] and may be related to this series.

The system Na_2O–P_2O_5–H_2O is illustrated in Fig. 1[204] which clearly shows the absence of the salt of formula $Na_3PO_4,12H_2O$.

The double compounds $Na_2SO_4,2Na_3PO_4$ and $Na_2SO_4,5Na_3PO_4$ have been identified at 200°C. in mixtures of the individual salts.[176] In the system Na_2O–P_2O_5–SiO_2 a stable compound $9Na_2O,2P_2O_5,6SiO_2$, m.p. 1100°C. and two peritectic compounds, $5Na_2O,P_2O_5,4SiO_2$, m.p. 953°C., and $15Na_2O,5P_2O_5,6SiO_2$, m.p. 987°C., forming various eutectics between themselves and with the binary compounds, have been reported.[205]

At 270°C., trisodium phosphate reacts with cyanogen, prepared *in situ* from silver cyanide, to give a 75% yield of sodium pyrophosphate but no sodium phosphite:-[206]

$$2Na_3PO_4 + (CN)_2 \rightarrow Na_4P_2O_7 + NaCN + NaCNO.$$

At 250° to 260°C. mixtures of normal sodium pyro- and ortho-phosphates give 20% yields of sodium triphosphate within 30 minutes.[207] Equimolecular mixtures of sodium dimetaphosphate and trisodium phosphate at 650° to 850°C. yield tetrasodium pyrophosphate:-[80,208]

$$Na_2P_2O_6 + 2Na_3PO_4 \rightarrow 4Na_4P_2O_7$$

In aqueous solutions, the formation of the two acid phosphates and phosphoric acid by the action of nitric acid on trisodium phosphate has been recognized thermometrically.[209] Dilute, but not concentrated, aqueous solutions of the salt dissolve small quantities of elemental sulphur with formation of greenish-yellow solutions which contain sulphide, polysulphide and thiosulphate ions.[210,211] Trisodium phosphate is said to act in an unspecified manner

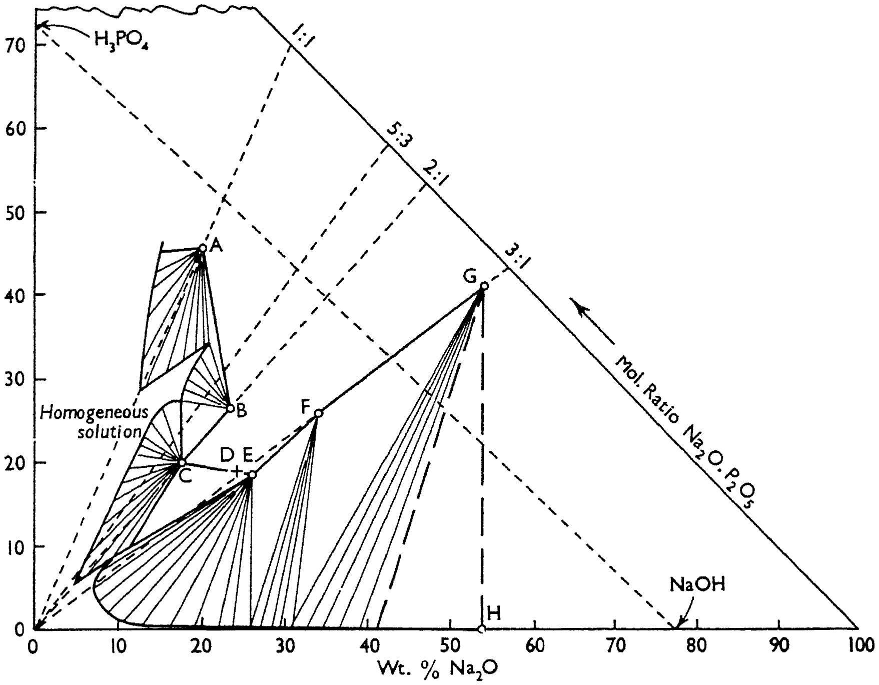

FIG. 1. THE SYSTEM NaOH-H_3PO_4-H_2O AT 25°C. AND 1 ATM.

as a mild preservative for solutions of hydrogen peroxide,[212] but it has no effect in the production of the peroxide by action of ultrasonic waves on oxygenated water.[213]

The precipitation reaction of silver nitrate with trisodium phosphate shows two tyndallimetric maxima corresponding to silver oxide and phosphate respectively.[214] The action of trisodium orthophosphate in the 'deliming' of hard waters has stimulated investigation into its action on solutions of calcium hydroxide, a 37·5% excess of which is required for complete precipitation of phosphate,[215] and on other soluble calcium salts.[115,216] It has been pointed out that the efficiency of commercial TSP is partly dependent on the presence of caustic soda which assists in the precipitation of calcium, for example as hydroxyapatites of the type $3Ca_3(PO_4)_2,Ca(OH)_2$.[217] The reaction of trisodium phosphate with cadmium and zinc salts has been examined.[218]

Addition of a solution of the salt to a solution of aluminium chloride is believed to lead to formation of a salt of the type $AlPO_4,Al(OH)Cl_2$, which, with further phosphate, is ultimately converted into the normal aluminium phosphate; addition of aluminium chloride to solutions of the trisodium phosphate gives rise to the following sequence of reactions:-[219]

$$6PO_4''' + Al^{\cdots} + 6H_2O \rightarrow Al(OH)_6''' + 6HPO_4''$$
$$Al(OH)_6''' + 6HPO_4'' + 5Al^{\cdots} \rightarrow 6AlPO_4 + 6H_2O$$

The precipitation reaction between trisodium phosphate and lead nitrate solutions has been studied for possible application to the titrimetric determination of lead; ion absorption[220] and non-agreement with the theoretical formula of the expected product, $Pb_3(PO_4)_2$,[221] have been invoked to explain high results obtained by this method. The reaction with bismuth nitrate under various conditions has been studied similarly.[222]

The corrosive action of TSP on glass[223] and on an anodic magnesium-aluminium alloy[224] has been investigated, but of much greater interest is the mechanism of its corrosion inhibition on ferrous surfaces: ferrous phosphate is thought to be the barrier formed but this disappears in the presence of excess sodium chloride;[153] in 0·1N. solutions, in the presence of air, sodium phosphate produces a deposit of a cubic oxide, Fe_3O_4, γ-Fe_2O_3 or an intermediate, together with some ferric phosphate[225-227] and this complex film is not removed by tartrate: in air-free solutions hydrated ferrous phosphate, $Fe_3(PO_4)_2,8H_2O$, is deposited and this is not sufficiently impermeable to prevent corrosion.[228]

The formation of $CH_3Na_2PO_4$ and $(CH_3)_2NaPO_4$ from trisodium phosphate and dimethyl sulphate at room temperature, and Na_2PO_4,C_2H_4OH,H_2O from the phosphate and $ClCH_2 \cdot CH(OH) \cdot CH_2OH$ has been reported.[229,230] Sodium phosphate has been suggested, *inter alia*, as a catalyst for the dehydration of 1:3-dihydroxyalkanes to di-olefines[231] and of dicarboxylic acids to their cyclic anhydrides[232] and in the reforming process for the production of naphthas.[233] Atmospheric oxidation of glucose has been shown to be increased in the presence of sodium phosphate[234] and the mutarotation of dextrose solutions in the presence of the salt has been studied.[235]

In simple solutions, sodium phosphate is usually determined acidimetrically[236] or electrometrically.[237] In more complex solutions use is made of anion exchange resin separations[190] or of the colour of sulphuric acid solutions of ammonium phosphomolybdate in acetone.[238]

Disodium Hydrogen Orthophosphate

Preparation.

The secondary sodium salt of orthophosphoric acid, Na_2HPO_4, is frequently made by the partial neutralization of phosphoric acid with a base such as sodium carbonate,[18,239-246] sometimes in the presence of ammonia,[247] or with a sodium salt of a volatile acid.[240] Alternatively, solutions of rock phosphate that has been digested with phosphoric acid or sulphuric acid, *i.e.*, solutions of the primary calcium phosphate $Ca(H_2PO_4)_2$, are treated with sodium carbonate,[248] with sodium sulphate followed by carbonate,[249] or with calcium hydroxide to form the secondary calcium phosphate $CaHPO_4$ which is then treated with sodium sulphate.[250] Again, the solution produced by attacking rock phosphates with nitric or hydrochloric acid can be treated with a cation exchange material in its sodium form.[251] Phosphate rocks when heated with sodium carbonate and carbon at red heat yield, on leaching the cooled cake with water, a solution from which sodium carbonate and disodium phosphate are recovered by treatment with carbon dioxide.[252] A laboratory preparation of the dodecahydrate from phosphoric acid and sodium hydroxide has been described in detail.[253] Disodium hydrogen phosphate has also been prepared by the action of trisodium orthophosphate[19] or sodium carbonate[254] on monosodium dihydrogen phosphate. The salt is said to be one of the thermal decomposition products of sodium triphosphate hexahydrate.[255] Solutions of disodium hydrogen phosphate are purified by careful control of pH which allows precipitation of tervalent cations,[242,256] by treatment with barium hydroxide to form secondary barium phosphate and barium sulphate both of which remove impurities by entrainment during their precipitation[257,258] and by treatment with sodium sulphide or hydrogen sulphide to remove heavy metal cations.[244] Laboratory separations from other sodium phosphates have been achieved by paper chromatography[259-262] and paper electrophoresis.[263] The aqueous solutions may be crystallized under different conditions to give the anhydrous salt or hydrates containing twelve, seven or two molecules of water:[264-271] the dodecahydrate is prepared by crystallization from water below 30°C.; the dihydrate by crystallization from hot (approximately 50° to 90°C.) solution or by dehydration of the dodecahydrate with boiling ethanol or on the steam-bath; the heptahydrate by fusing together calculated quantities of the dodeca- and di-hydrates or by heating the dodecahydrate to 35° to 40°C.; and the anhydrous salt by crystallization of the solution, or by heating any hydrate, above 96°C.

Uses.

The use of disodium hydrogen phosphate for the preparation of sodium pyrophosphate and of buffer solutions is discussed later. Other applications of the salt include: as a deterrent to corrosion,[272,273] especially by brine[274] and sulphate solutions,[275] although water-line attack may be severe in the presence of oxygen;[276] for the preparation of other protective coatings;[150,277-279] in the fire-proofing of timber[280,281] and in the pulping of wood;[282] as a constituent of binders for moulds used in precision metal casting,[283] for metal-working lubricants;[284] and as a minor constituent of detergents.[95,285] It is commonly used as a source of soluble phosphate, for example in the purification of soluble compounds from cations which form insoluble phosphates;[286,287] the possible use of the dodecahydrate as a heat-pump medium has been discussed;[288] added to vinyl resins, the salt is said to improve their heat and light stability,[289-291] and it has been used as an additive to dried milk,[292-294] and to butter[295] but not successfully in cheese.[296]

Physical Properties.

The transition (invariant) points in the hydrate systems of disodium hydrogen phosphate have been determined thermometrically[264] and viscometrically[297] as follows:-

β-$Na_2HPO_4,12H_2O \rightarrow \alpha$-$Na_2HPO_4,12H_2O$	29·6°C.[264]
α-$Na_2HPO_4,12H_2O \rightarrow Na_2HPO_4,7H_2O$	35·0°C.[264] 35·6°C.[297]
$Na_2HPO_4,7H_2O \rightarrow Na_2HPO_4,2H_2O$	48·09°C.[264]
$Na_2HPO_4,2H_2O \rightarrow Na_2HPO_4$	94·97°C.[264]

and the complete system is shown as a heating curve in Fig. 2. The β-dodecahydrate and ice form a eutectic with ice at −0·47°C. This wide range of hydrates, interconvertible at relatively low temperatures, is inconvenient and recipes have been given for producing lower (usually di-) hydrates which have satisfactory storage properties.[298-300] Dehydration of the salt by means of anhydrous dioxan has been studied physicochemically.[301] The dissociation pressure (p) and heat of reaction (Q) data for the dehydration reactions are summarized in Table IV.

TABLE IV. - DISSOCIATION PRESSURE AND HEAT OF REACTION DATA FOR DISODIUM HYDROGEN PHOSPHATE HYDRATES

Reaction				
$Na_2HPO_4, 12H_2O \rightleftharpoons Na_2HPO_4, 7H_2O + 5H_2O$		$Na_2HPO_4, 7H_2O \rightleftharpoons Na_2HPO_4, 2H_2O + 5H_2O$		
Temperature (°C.)	Pressure (mm.)	Temp. (°C.)	Pressure (mm.)	Q[305] (g.-cal./mol.)
0·0	2·66[302]	10·0	4·55[305]	12,140
14·9	8·93[303]	15·0	6·81[305]	12,160
15·0	8·93[302]	20·0	10·04[305]	10,010
20·0	12·98[303]	25·0	14·41[305] 14·51[304]	
24·92	19·10[303]			
25·0	19·04[302] 19·13[304]			
30·0	27·05[303]			

The apparent density of the powdered phosphate is given as 1·01.[168]

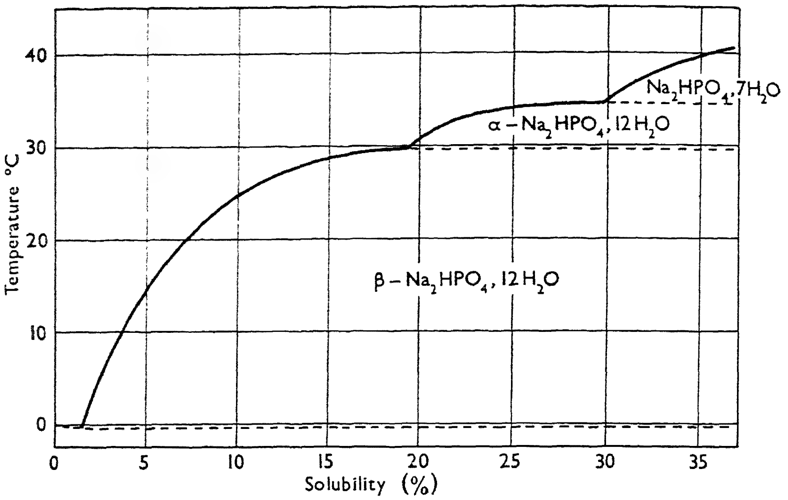

FIG. 2. SOLUBILITY OF THE HYDRATES OF DISODIUM HYDROGEN PHOSPHATE

Infra-red absorption data for the powdered dihydrate and anhydrous salt are given in Table V.[171]

TABLE V.- INFRA-RED ABSORPTION OF DISODIUM HYDROGEN PHOSPHATE[171]

Salt			
Na_2HPO_4		$Na_2HPO_4, 2H_2O$	
Wave number (cm.$^{-1}$)	Intensity	Wave number (cm.$^{-1}$)	Intensity
2570	weak, broad	3450	strong
1350	weak	3360	strong
1310	weak	3080	strong
1240	weak	2700	weak, broad
1148	strong	1700	weak, broad
1125	strong	1257	medium
1100	strong	1133	strong
1065	strong, broad	1120	strong
991	strong	1067	strong
973	medium	990	medium
940	broad	950	strong
~850	strong, broad	862	medium
798	medium	815	weak

The dielectric constant of the anhydrous powder is reported as 8·5 as a minimum value,[174] and for the dodecahydrate, perpendicular to the (001) axis, 5·2, with a temperature coefficient of 3×10^{-3} but with no appreciable anisotropy. From the coefficient, the energy of activation is deduced as 13 kg.-cal./mole.[306] The molecular magneto-optical rotatory power is −566, of which −353 is contributed by the phosphate ion.[307]

Selected values for the solubility of the salt in water are given in Table VI. Osmotic and activity coefficients of various concentrations of the salt are listed in Table III[181] (see page 1265).

TABLE VI. - SOLUBILITY OF DISODIUM HYDROGEN PHOSPHATE IN WATER

Temperature (°C.)	Solubility (%)[264]
−0·47	1·45
0·0	1·631g./100g. of water[308]
6·00	2·73
11–12	11·5[309] (dodecahydrate)
18·0	6·367g./100g. of water[308]
22·77	8·93
24·15	9·53
25·0	12·144g./100g. of water[308]
25·75	10·90
27·80	14·16
29·50	17·18
30·10	19·45
32·50	22·57
34·70	29·75
36·50	31·15
40·02	35·56

Comprehensive data on the density of solutions of the dodecahydrate at different concentrations and temperatures have been published.[310] Hydrogen peroxide increases the solubility of the salt at 0°C., an effect probably due to formation of double salts.[308] It has been observed that glycerol decreases the solubility of disodium hydrogen phosphate in water, but it does not affect the nature of the crystallizing product except in high concentrations of glycerol when glyceroxides are formed.[311] The isotherms of the system Na_2HPO_4-K_2HPO_4-H_2O have been examined at 0° and 25°C.: there is evidence for the formation of a salt $NaKHPO_4,5H_2O$ in the solid phase.[312] The final heat of solution of the dodecahydrate at 11–12°C. has been given as −21·845[309] or −21·79[313] g.-cal.

Partition chromatography on cellulose has been employed as a means of separating many phosphates of sodium:[260,262,263] Table VII[259,261] gives R_f values that have been published for several of the sodium phosphates in various solvents. The absolute diffusion coefficient for disodium hydrogen phosphate in 1·0% gelatin has been found by radiotracer technique[314] to be $0{\cdot}413 \times 10^{-5}$ c.g.s. units at 18°C. for 0·05N. solutions and $0{\cdot}365 \times 10^{-5}$ units at 17°C. for 0·01N. solutions. At infinite dilution the value given for the hydrogen phosphate ion is $5{\cdot}10 \times 10^{-6}$ units.[315] Self diffusion coefficients are given as $2{\cdot}98 \times 10^{-6}$ c.g.s. units in 0·5M. and $5{\cdot}1 \times 10^{-6}$ units in 0·001M. solutions at 20°C.[316] Dialysis of the salt through cellophane has been studied.[317]

A wide range of data on refractive indices of the solutions of the dodecahydrate has been published.[318]

The use of the salt as a reference compound in the pH scale is common and various publications[319-323] have critically reviewed its application and given extensive tables of information. Of particular value are the data for equimolal solutions with potassium dihydrogen phosphate given by Bates and Acree[324] some of which are summarized in Table VIII (changing molality) and Table IX (effect of temperature) and in Figs. 3 and 4. In these solutions at 25°C., pH may be represented by the following equations:-

$$\mathrm{pH} = 7{\cdot}162 + 2{\cdot}18m - 2{\cdot}237m^{1/2} \text{ or } \mathrm{pH} = 7{\cdot}169 + 2{\cdot}39c - 2{\cdot}324c^{1/2}$$

TABLE VII. - R_f VALUES FOR SODIUM PHOSPHATES ON CELLULOSE

Salt	Solvent (parts by volume)			
	I (a)[259] iso-C_3H_7OH 70 H_2O 30 CCl_3COOH 5	(b)[261] 75 25 5	II[259] tert.-C_4H_9OH 40 iso-C_3H_7OH 30 H_2O 30 CCl_3COOH 5	III[259] tert.-C_4H_9OH 80 H_2O 20 $C_6H_2(NO_2)_3OH$ 4
Na_2HPO_4	0·76	0·68	0·72	0·68
$(NaPO_3)_3$	0·56		0·55	0·49
$(NaPO_3)_4$	0·44		0·49	0·38
$Na_4P_2O_7$	0·34		0·44	0·34
$Na_5P_3O_{10}$	0·22		0·38	0·48
$(NaPO_3)_6$	0·0		0·0	0·0

Salt	Solvent (parts by volume)	
	IV[259] tert.-C_4H_9OH 20 iso-C_3H_7OH 40 H_2O 39 aq.NH_3 1	(a)[259] (b)[261] iso-C_3H_7OH 30 – tert.-C_4H_9OH – 30 C_2H_5OH 30 30 H_2O 39 39 aq.NH_3 1 1
Na_2HPO_4	0·43	0·45
$(NaPO_3)_3$	0·33	0·36
$(NaPO_3)_4$	0·30	0·30
$Na_4P_2O_7$	0·54	0·74
$Na_5P_3O_{10}$	0·48	0·61
$(NaPO_3)_6$	0·0	0·0

where m is molality and c is molarity. The effect of added sodium chloride is shown in Fig. 5. Other published values for the equimolecular solutions with potassium dihydrogen phosphate are: at 0·025M. with respect to each salt, pH is 6·835 and 6·855 at 25° and 38°C. respectively;[325] at 0·2M., pH is 6·8 at room temperature.[326]

TABLE VIII. - pH OF EQUALMOLAL SOLUTIONS OF DISODIUM HYDROGEN PHOSPHATE WITH POTASSIUM DIHYDROGEN PHOSPHATE AT 25°C.[324]

Mole of each salt	Concentration (g./l.)		pH (25°C.)
	KH_2PO_4	Na_2HPO_4	
0·005	0·6805	0·7099	7·018
0·01	1·361	1·420	6·959
0·02	2·722	2·840	6·886
0·025	3·402	3·550	6·860
0·04	5·444	5·680	6·802
0·05	6·805	7·099	6·772
0·075	10·21	10·65	6·714
0·1	13·61	14·20	6·671

Alone, disodium hydrogen phosphate has a pH of 8·59 at a concentration of 0·1M. and this is decreased by approximately 0·27 pH units for every 0·1M. increase of sodium fluoride concentration.[327] The citric acid-disodium hydrogen phosphate buffer solution has received some attention[328] with regard to dilution of the system, and selected data are presented in Table X.[329] The

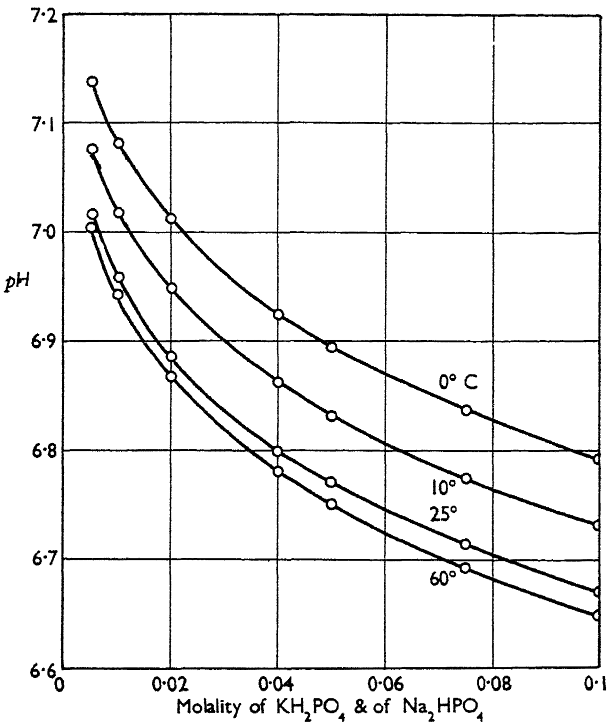

FIG. 3. pH OF PHOSPHATE BUFFERS AS A FUNCTION OF MOLALITY AT 0°, 10°, 25° AND 60°C.

TABLE IX. - EFFECT OF TEMPERATURE ON THE pH OF EQUIMOLAR SOLUTIONS OF POTASSIUM-DIHYDROGEN PHOSPHATE AND DISODIUM HYDROGEN PHOSPHATE[324]

Temperature (°C.)	pH values at the following concentrations					
	0•005	0•01	0•025	0•05	0•075	0•1
0	7•138	7•081	6•983	6•895	6•836	6•792
10	7•077	7•019	6•922	6•832	6•776	6•732
15	7•053	6•995	6•896	6•808	6•750	6•706
20	7•034	6•976	6•878	6•791	6•733	6•690
25	7•018	6•959	6•860	6•772	6•714	6•671
30	7•007	6•948	6•849	6•760	6•702	6•658
40	6•996	6•937	6•837	6•748	6•690	6•647
50	6•995	6•934	6•833	6•743	6•684	6•640
60	7•002	6•941	6•840	6•749	6•691	6•647

buffer is effective over the range 2•10 to 9•01 pH units, depending on the concentration of the components.[329] A similar buffer solution of disodium hydrogen phosphate and glycine in conjunction with hydrochloric acid and sodium hydroxide has been proposed for the pH range 6•93 to 11•91: data are summarized in Table XI, in which measurements are recorded for solutions of approximately constant (~0•5M.) ionic strength of potassium chloride.[330]

Most quantitative determinations of the salt in simple solutions are based on acidimetric titration.[331,332]

The physical effects of disodium hydrogen phosphate on several other

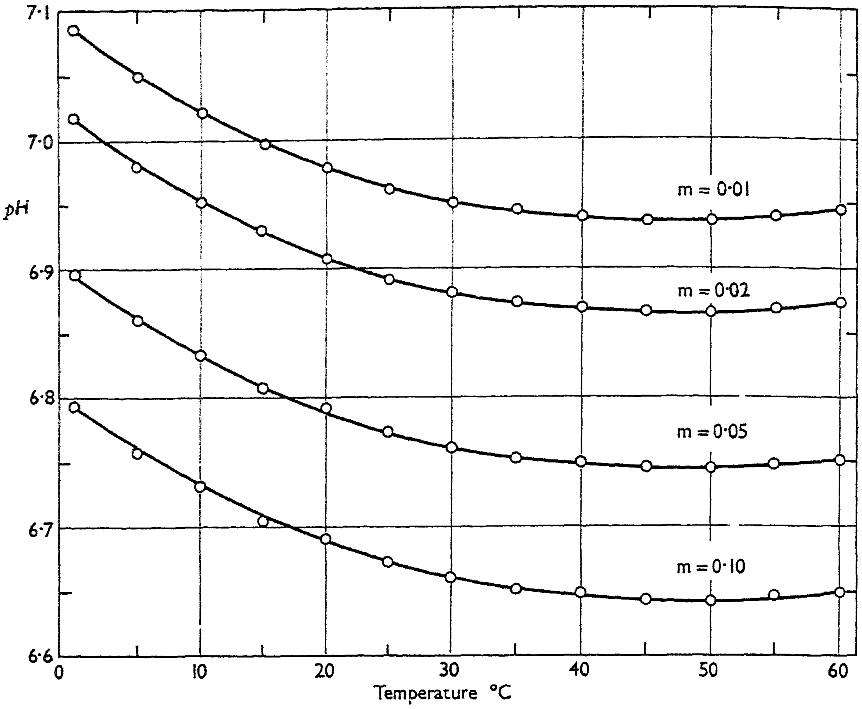

FIG. 4. pH OF FOUR PHOSPHATE BUFFERS AS A FUNCTION OF TEMPERATURE

TABLE X. - THE CITRIC ACID-DISODIUM HYDROGEN PHOSPHATE BUFFER[329]

Millilitres of 0·1M. citric acid added	Millilitres of 0·2M. disodium phosphate added	pH values at:			
		20°	25°	35°	45°C.
0	20	9·01	8·94	8·89	8·87
2	18	7·36	7·38	7·41	7·47
4	16	6·89	6·91	6·93	6·99
6	14	6·40	6·42	6·49	6·57
8	12	5·70	5·74	5·82	5·90
10	10	4·89	4·91	4·98	5·07
12	8	4·10	4·12	4·19	4·28
14	6	3·50	3·52	3·59	3·68
16	4	3·01	3·05	3·12	3·21
18	2	2·51	2·55	2·63	2·71
20	0	2·10	2·14	2·19	2·24

The temperature coefficient is constant between the temperatures listed.

systems have been investigated. Thus, in the Ag_3PO_4-Na_2HPO_4-H_2O system, an increase of sodium phosphate concentration from zero to 0·829M. decreased the solubility product of silver phosphate from $1{\cdot}83 \times 10^{-10}$ to $1{\cdot}21 \times 10^{-13}$ without greatly affecting the activity coefficient;[333] the effect of the salt on the solubility of boric acid in water has been found to follow an expression $\log S = \log S_0 + k/c$ where S is solubility of the acid and c the concentration of sodium phosphate;[334,335] the exchange of phosphate ions between tricalcium phosphate and a solution of disodium phosphate has been demonstrated to take

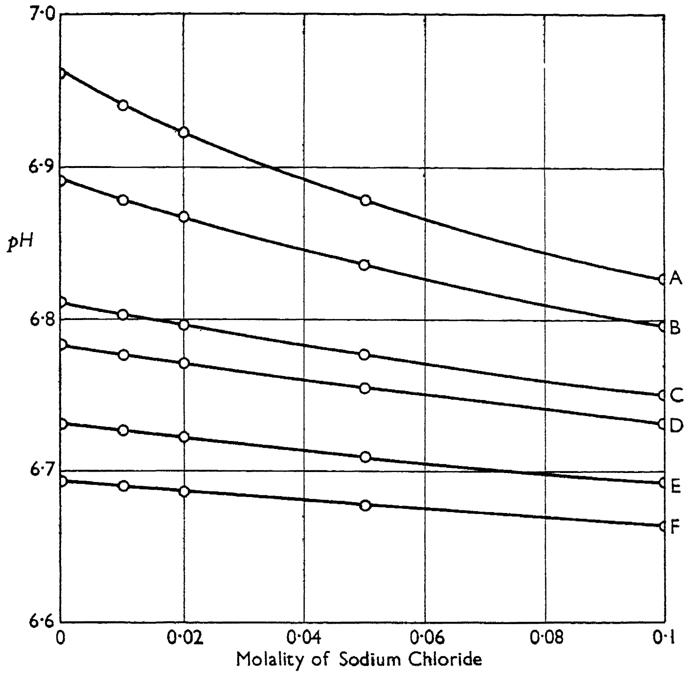

FIG. 5. EFFECT OF SODIUM CHLORIDE ON THE pH OF SIX PHOSPHATE BUFFERS

Curves A, B, C, D, E and F represent buffers in which both phosphates are respectively 0·01, 0·02, 0·04, 0·05, 0·075 and 0·1 molal.

TABLE XI. - EFFECT OF ADDITION OF HYDROCHLORIC ACID AND OF SODIUM HYDROXIDE ON A SOLUTION 0·05M. WITH RESPECT TO GLYCINE AND TO DISODIUM HYDROGEN PHOSPHATE[330]

Hydrochloric acid (molality)	Sodium hydroxide (molality)	pH values at:			
		20°	25°	30°	35°
0·015	0·000	6·95	6·93	6·91	6·90
0·009	0·000	7·23	7·21	7·20	7·18
0·004	0·000	7·61	7·58	7·55	7·52
0·001	0·000	8·016	7·955	7·904	7·853
0·000	0·000	8·184	8·104	8·034	7·944
0·000	0·002	8·52	8·42	8·32	8·24
0·000	0·004	8·79	8·65	8·53	8·42
0·000	0·009	9·15	9·01	8·88	8·77
0·000	0·020	9·61	9·47	9·33	9·22
0·000	0·031	9·97	9·83	9·71	9·59
0·000	0·042	10·33	10·20	10·09	9·98
0·000	0·050	10·62	10·50	10·40	10·31
0·000	0·063	11·07	10·96	10·88	10·80
0·000	0·075	11·41	11·30	11·22	11·14
0·000	0·088	11·75	11·63	11·54	11·44
0·000	0·100	12·05	11·91	11·79	11·68

place in three kinetically separable steps;[336] in common with all other orthophosphates, oxygen exchange in the phosphate ion was shown to be non-existent;[337] the salt has been taken as an example of the behaviour of simple salts in depressing the freezing point of saturated aqueous sodium sulphate[338] and has been used in the determination of degree of hydration of salts by an organic dye partition method.[339] The dispersing action of the salt on lead arsenate,[340] its effect on the ζ-potential of, e.g., lampblack,[341] and on the thermal coagulation of casein[342] have been investigated; studies have also been made on the influence of disodium phosphate on the electrolysis of sodium acetate solutions,[343] on the urea-formaldehyde condensation reaction,[344] on the interconversion of certain hexoses,[345] on the urease-catalyzed hydrolysis of urea[346] and on the fermentation of molasses to 2:3-butandiol with various agents,[347] in the last two of which it can play an active part. The salt is believed to influence ingested meat metabolism,[348] to decrease the calcium content of blood after injection[349] and, in conjunction with vitamin A, to prevent stone formation in the urinary tract of rats;[350] in pot experiments, but not, apparently, in the field, the salt can improve rice yields.[351]

The partial pressures of the system Na_2HPO_4-NaH_2PO_4-SO_2-H_2O between 30° and 90°C. have been measured: sulphur dioxide absorption increases with increasing phosphate concentration and with increasing sodium to phosphate ratio. 100 ml. of a solution 9·05 molar with respect to phosphate ion, with a sodium to phosphate ratio of 1·64 to 1, absorbs 64g. of sulphur dioxide per litre from a gas containing 0·3% of sulphur dioxide; the gas can be removed by boiling, except from concentrated phosphate solutions.[352,353]

Chemical Properties.

Thermal dehydration of the hydrated disodium hydrogen phosphates results in loss of the water molecules of hydration followed by the loss of 'molecular' water to give tetrasodium pyrophosphate with no known intermediate products.[354] The dissociation pressures of the reaction have been measured;[355] the decomposition temperature of the reaction is stated to be unaffected by external pressure.[356] Action of heat on the double salt $Na(NH_4)HPO_4$, m.p. 79°C., causes decomposition at 96°C. with formation of a metaphosphate at 320°C. *via* an intermediate pyrophosphate, $Na_2NH_4HP_2O_7$, found at 220°C.[354] Similarly, at 200°C., a mixture of disodium hydrogen phosphate and ammonium nitrate leads to the formation of disodium dihydrogen pyrophosphate:-[357]

$$2Na_2HPO_4 + 2NH_4NO_3 \rightarrow Na_2H_2P_2O_7 + 2NaNO_3 + 2NH_3 + H_2O$$

which decomposes to the normal metaphosphate at higher temperatures.

Thermal dehydration of mixed crystals of disodium phosphates and arsenates, $Na_2H(P,As)O_4$ gives the corresponding diarsenatophosphates, $Na_4(P,As)_2O_7$, provided that the arsenic to phosphorus ratio exceeds 1:1, but triarsenatophosphates, e.g., $Na_3H_2(P,As)_3O_{10}$ are formed above 192°C. when the ratio is increased to $\geqslant$2:1.[358] Disodium hydrogen phosphate reacts slowly with an equimolecular mixture of trisodium hydrogen pyrophosphate, e.g., that formed in the pyrolysis of sodium triphosphate hexahydrate, at or above 120°C. to give anhydrous sodium triphosphate.[255]

Heating equimolecular mixtures of sodium bisulphate and disodium hydrogen phosphate causes an exothermic reaction forming the normal sulphate and monosodium dihydrogen phosphate which is then able to form its normal dehydration products at higher temperatures: there is no evidence for the formation of such compounds as sulphatophosphates in this mixture.[359]

Radioactive pyrophosphates and phosphites have been detected after neutron irradiation of the anhydrous salt or its dihydrate.[360]

In aqueous solution, several reactions with other inorganic salts have been examined. The reaction with lithium ions, used as a method of detecting these cations, has been made more sensitive by the addition of triethanolamine.[361] Precipitation of silver phosphate from silver nitrate and disodium phosphate in the presence of pyramidone and benzene has been suggested as an argentometric method for the determination of phosphate.[362] The presence of disodium phosphate is necessary in the formation of Liesegang rings of silver chromate in agar.[363] The aqueous reaction between disodium phosphate and calcium chloride has been shown not to yield the pure secondary calcium phosphate, $CaHPO_4$, owing to simultaneous formation of, e.g., hydroxyapatite;[364] the setting of plaster of Paris is retarded owing to the precipitation of such salts and to the prevention of supersaturation in the presence of the phosphate.[365,366] The periodic reaction of the salt with calcium chloride in gelatin has been investigated:[367] the relationship λV = constant ($\simeq 2{\cdot}5 \times 10^{-6}$ cm.^{2}/sec.), where λ is the distance between rings and V is the spreading velocity of the diffusion field, is said to describe the phenomenon.[368] The action of mercuric chloride on solutions of disodium phosphate has been shown to yield a red-brown precipitate of basic mercuric salts such as $2HgO,HgCl_2$ (red) at 30° to 40°C. and $3HgO,HgCl_2$ (black) at 90°C.[369] probably mixed with a yellow-white intermediate which is, perhaps, the basic phosphate $HgO,Hg_3(PO_4)_2$.[370] Compounds such as the double salts $Hg_3(PO_4)_2,Na_2HPO_4$, *d* 6·25, and $Hg_3(PO_4)_2,Na_2HPO_4,2H_2O$ at 50° to 90°C., $Hg_3(PO_4)_2,Na_2HPO_4,7H_2O$ at 40°C. and $HgO,Hg_3(PO_4)_2$, *d* 7·883, at 30° to 36·4°C., usually mixed with normal mercuric phosphate, are produced on mixing 0·1 and 0·2M. solutions of mercuric nitrate with M. solutions of disodium phosphate in varying proportions at the various temperatures given.[371]

The reactions between secondary sodium orthophosphate added to aqueous aluminium chloride and *vice versa* appear to follow the courses:-[219]

1. $Al^{\cdot\cdot\cdot}(\text{excess}) + HPO_4'' \rightarrow AlPO_4 + H^{\cdot}$ followed by
   $HPO_4'' + H^{\cdot} \rightarrow H_2PO_4'$
2. $2HPO_4''(\text{excess}) + Al^{\cdot\cdot\cdot} \rightarrow AlPO_4 + H_2PO_4'$ and
   $H_2PO_4' + Al^{\cdot\cdot\cdot} \rightarrow AlPO_4 + 2H^{\cdot}$

The precipitation titration of lead with disodium hydrogen phosphate solution has been shown to lead to high results owing to ion adsorption[220] and non-agreement with the expected formula of the lead phosphate product.[221]

In the inhibition of corrosion by disodium hydrogen phosphate, γ-ferric oxide has been shown to be the effective surface product on steels, resulting from the sequence: $Fe^{\cdot\cdot} + 2OH' \rightarrow Fe(OH)_2 \rightarrow \gamma\text{-}Fe_2O_3,H_2O \rightarrow$ Intermediate $\rightarrow \gamma\text{-}Fe_2O_3$.[372] Ferric phosphate may also be formed at lower hydrogen ion concentrations.[226,227]

From mixed solutions of disodium phosphate and hydrogen peroxide a compound $Na_2HPO_4,2H_2O_2$, stable at 70°C. *in vacuo* but decomposed at 130°C., has been isolated at 0°C. Evidence for the unstable compound $Na_2HPO_4,2H_2O_2,10H_2O$ was also found.[308]

Monosodium Dihydrogen Orthophosphate

Preparation.

Primary sodium phosphate is prepared by one of several methods: (*a*) by treatment of phosphoric acid with sodium chloride to produce the acid salt NaH_2PO_4,H_3PO_4 from which the sodium phosphate is precipitated with ethanol or methanol and the phosphoric acid and alcohol are recovered for further use;[373,374] (*b*) by careful control of the sodium to phosphate ratio, the salt can be prepared from phosphoric acid and sodium hydroxide or carbonate;[246] (*c*) by heating equimolecular mixtures of sodium chloride with any of the acid ammonium orthophosphates at 250° in the presence of steam a yield of the salt of 79% is obtained within 6 hours;[375] (*d*) by treating dicalcium phosphate, derived from the action of sulphuric acid on rock phosphates for example, with aqueous sodium oxalate[376] or sulphate,[377] followed by removal of the calcium ions as the insoluble oxalate or sulphate; (*e*) by treatment of disodium hydrogen orthophosphate with cold sulphuric acid, the resulting sodium sulphate being removed as Glauber's salt below 32°C.[378] or with barium carbonate[379] and the monosodium phosphate then crystallized from the mother liquor; (*f*) by the analogous method of heating ferrophosphorus with sodium carbonate or sulphate and treating the resulting trisodium orthophosphate with phosphoric acid;[380] (*g*) it has been proposed to use the reaction between borax and phosphoric acid for the production of both sodium dihydrogen phosphate and boric acid.[381] When these processes are conducted on a large scale the resulting solutions of the salt are treated, for example, by autoclaving with disodium hydrogen phosphate to remove calcium[287] ($\mathrm{Ca^{\bullet\bullet}} + \mathrm{HPO_4''} \rightarrow \mathrm{CaHPO_4}$) and with hydrated alumina to remove fluoride,[382] and the purified solutions are evaporated and allowed to crystallize.

In the laboratory, the monohydrate may be prepared by the action of sodium bicarbonate[383,384] on aqueous phosphoric acid, followed by crystallization of the salt from water. Sodium dihydrogen phosphate is said to be present in the mixtures obtained on heating sodium triphosphate hexahydrate at 85° to 120°C.[385] and on heating mixtures of sodium bisulphate and disodium hydrogen phosphate.[359] The salt has been shown to be the ultimate product in the acid hydrolysis of dilute aqueous solutions of several of the condensed sodium phosphates.[83]

Uses.

Probably the main use of the monosodium phosphate today lies in its thermal decomposition to the acid pyrophosphate and the wide range of sodium metaphosphates which find many applications in water treatment. This reaction and its application are discussed more fully below. Other uses include: as a constituent of pH and buffer solutions;[384,386] in paper size manufacture;[387,388] in phosphatizing baths for metal objects;[150,389,390] in mould coatings used in the casting of metals;[391,392] as a constituent of fire-proofing recipes;[393,394] in hair setting agents;[395] in solutions used for the recovery of fatty acid oils;[396] in flocculating agents used for clarifying alkyd resins;[397] as a condensing agent in organic synthesis;[398] and in the electrolytic production of sodium perborate.[399]

Physical Properties.

The apparent density of the powder has been given as 1·31.[168] Infra-red absorption characteristics of the dihydrate and the anhydrous salt are given in Table XII.[171]

TABLE XII.- INFRA-RED ABSORPTION OF MONOSODIUM HYDROGEN PHOSPHATE[171]

$\mathrm{NaH_2PO_4}$		$\mathrm{NaH_2PO_4,2H_2O}$	
Wave number (cm.$^{-1}$)	Type	Wave number (cm.$^{-1}$)	Type
~2750	medium, broad	3500	broad
1650	medium	3420	broad
1300	medium	3250	broad
1282	medium	2700	weak, broad
1160	strong	1658	medium
1125	strong	1280	medium, sharp
1045	strong	1245	medium
981	strong, broad	1163	strong
927	strong, broad	1100	strong
870	medium	1040	strong
815	very weak	~990	weak, sharp

continued on following page

TABLE XII (continued)

NaH_2PO_4		$NaH_2PO_4, 2H_2O$	
Wave number (cm.$^{-1}$)	Type	Wave number (cm.$^{-1}$)	Type
		958	strong
		903	strong
		888	weak, sharp
		820	very weak

Measurement of the dielectric constant at 9500Mc. shows that anhydrous and hydrated monosodium dihydrogen phosphate undergo no phase transitions over the range 50° to 300°K.,[400] but conductometric measurements indicate a transition zone at approximately 400°C.[401] The effect of temperature on the dielectric constant has been examined in detail[168] and a minimum value at room temperature of 6·44 for the anhydrous salt has been recorded.[174] Investigation of the specific inductive capacities (ϵ) gave the following data:-[402]

Orientation	ϵ	Refractive index
p (001)	6·84	n_g 1·481
g'(010)	5·60	n_m 1·463
h'(100)	5·60	n_p 1·440

Therefore the crystals are uniaxial with an anisotropic difference of 1·24; whereas the quoted data for the refractive index for the same crystal indicate biaxial characteristics. The Raman spectra of the dihydrate and of solutions of the salt have been measured and compared.[403]

Viscometric examination of the fused system sodium borate–sodium dihydrogen phosphate gave no indication of complex compound formation: for mixtures containing 25% of borax, viscosities are given as 15·7 poise at 732° and 38,370 poise at 532°C.[404]

For the anhydrous salt, the monohydrate and the dihydrate, 1·05, 0·79 and 0·58 c.c. respectively of water are required to dissolve one gram of the salt.[405] The true dissociation constant is given as $2{\cdot}67 \times 10^{-7}$,[386] and this has been incorporated in a formula for deducing the pH of buffer solutions of the salt. The determination of sodium dihydrogen phosphate in simple solutions or mixtures is usually performed alkalimetrically.[406] A selection of data on osmotic and activity coefficients is given in Table XIII.[407]

TABLE XIII.- OSMOTIC AND ACTIVITY COEFFICIENTS OF SOLUTIONS OF MONOSODIUM DIHYDROGEN ORTHOPHOSPHATE[407]

Molarity	Coefficients	
	Osmotic	Activity
0·1	0·911	0·744
0·2	0·884	0·675
0·5	0·832	0·563
0·8	0·798	0·499
1·0	0·780	0·468
1·6	0·739	0·401
2·0	0·721	0·371
3·0	0·696	0·320
5·0	0·699	0·276

It was concluded that the data in Table XIII could be represented by an extended Debye–Hückel equation and that the salt could undergo ion-pair formation as do other oxy-salts. Other data have been given in Table III[181] (see page 1265). In aqueous solutions the self diffusion coefficient ($D \times 10^6$) has been determined as 7·30 - 0·363log c, where c is concentration in g.mol./l., over the range 10^{-4} to 10^{-1} molar, with $D_0 = 8{\cdot}9 \times 10^{-6}$cm.^{2}sec.$^{-1}$ at infinite dilution. In higher concentrations (10^{-1} to 1M.) the rapid rise in the coefficient is probably due to the relatively small change of viscosity coefficient in this range.[408,409] The diffusing ion above 0·005M. is H_2PO_4', but below this concentration HPO_4'' contributes to the diffusion; the activation energy of self diffusion is given as 4·3 kg.-cal./mole at infinite dilution and 5·4 kg.-cal./mole at 0·9M. (cf. 4·6 and 4·8 kg.-cal./mole respectively, calculated from viscometric data).[409] In the expression $\gamma_m = (a + h)/(b + h)$, where h is the reciprocal of the concentration in g.-mol./l., a and b are found to be 12·90 and 19·57 respectively at 9° to 11°C. for the dihydrate.[410] The effect of sodium dihydrogen phosphate on the freezing point lowering of saturated solutions of sodium sulphate has been discussed.[338]

The following effects of aqueous solutions of the salt on various other systems have been described: coagulation of several inorganic colloids;[411] sedimentation of lime;[412] solubility of calcium gluconate;[413] association of insulin molecules;[414] the excretions of the human body[415] and its capacity for work;[416] infection of eggs with influenza virus.[417] The salt promotes the catalytic action of cupric ions in the iodide-persulphate reaction,[418] and the rate of oxidation of ferrous ions in aqueous solution by oxygen at an ionic strength of 1 to 1·1M. with respect to sodium perchlorate is given[419] as:-

$$\frac{-d[Fe^{\bullet\bullet}]}{dt} = k[Fe^{\bullet\bullet}][H_2PO_4']^2 p_{O_2}$$

where k at 30°C. is 4·5 litres^{2}atm.$^{-1}$mole^{-2}hr.$^{-1}$

Chemical Properties.

The action of heat on monosodium dihydrogen phosphate has received considerable attention.[354,420,421] The weight losses with increasing temperature are shown in Fig. 6[422] which indicates the possible formation of a monohemihydrate, followed by complete loss of hydration and then molecular loss of water with formation of disodium dihydrogen pyrophosphate and finally the sodium metaphosphates (q.v.):-

$$2NaH_2PO_4,2H_2O \xrightarrow[33\text{-}40°]{} 2NaH_2PO_4,1{\cdot}5H_2O \xrightarrow[70\text{-}80°]{} 2NaH_2PO_4 \xrightarrow{198\text{-}206°}$$
$$Na_2H_2P_2O_7 \xrightarrow[298\text{-}338°]{} 2\text{'}NaPO_3\text{'} \xrightarrow[610°]{} NaPO_3 \text{ glass.}^{423}$$

The dissociation pressures of the reaction $2NaH_2PO_4 \rightleftharpoons Na_2H_2P_2O_7$ are given in Table XIV.[355]

TABLE XIV. - DISSOCIATION PRESSURES OF THE REACTION $2NaH_2PO_4 \rightleftharpoons Na_2H_2P_2O_7$[355]

Temperature (°C.)	Pressure (mm.)
110	17·9
120	36·1
130	66·1
140	245·0
145	360·0
148	521·0
150	750·0

In the presence of phosphoric acid at 300°C. sodium dihydrogen phosphate gives disodium dihydrogen tetrametaphosphate:[424]

$$2NaH_2PO_4 + 2H_3PO_4 \rightarrow Na_2H_2(PO_3)_4 + 4H_2O$$

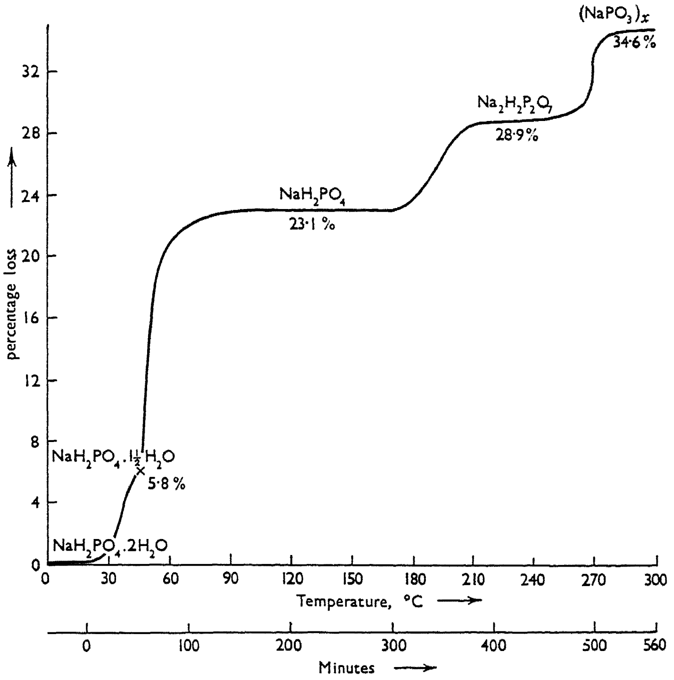

FIG. 6. THERMOGRAVIMETRIC EXAMINATION OF MONOSODIUM DIHYDROGEN ORTHOPHOSPHATE DIHYDRATE

or a disodium hydrogen trimetaphosphate polymer:-

$$2n\mathrm{NaH_2PO_4} + n\mathrm{H_3PO_4} \rightarrow [\mathrm{Na_2H(PO_3)_3}]_n + 3n\mathrm{H_2O}$$

When heated in air, below 400°C., mixtures of alkali metal iodides and dihydrogen sodium phosphate afford a convenient method of preparing free iodine.[80]

The adsorption of sodium dihydrogen phosphate on alumina is ascribed to the following mechanism[425] in nitrate solution:-

$$(\mathrm{Al_2O_3})_m\mathrm{AlO^+NO_3{}'} + \mathrm{H_2PO_4{}'} \rightleftharpoons (\mathrm{Al_2O_3})_m\mathrm{AlO^+H_2PO_4{}'} + \mathrm{NO_3{}'}$$

and for the sodium ion adsorption:-

$$(\mathrm{Al_2O_3})_m\mathrm{AlO^+H_2PO_4{}'} + \mathrm{NaOH} \rightleftharpoons (\mathrm{Al_2O_3})_m\mathrm{AlO^+OH'} + \mathrm{NaH_2PO_4}$$
$$\mathrm{NaH_2PO_4} + \mathrm{NaOH} \rightleftharpoons \mathrm{Na_2HPO_4} + \mathrm{H_2O}$$

The scheme has been extended to the study of soils. Kaolinite gives a compound $\mathrm{H_{1\cdot7}Na_{1\cdot2}Al_{2\cdot0}Fe_{0\cdot004}(PO_4)_3,2\cdot7H_2O}$ in M. aqueous sodium dihydrogen phosphate[426] at pH 4·3 and at 90°C. The effect of the salt on the solubility of boric acid in water has been studied experimentally and theoretically;[334,335] in concentrated solutions complex borophosphates may be formed.[427]

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SODIUM POLYPHOSPHATES

Sodium Pyrophosphates, Sodium Diphosphates

Tetrasodium Pyrophosphate, Normal Sodium Diphosphate

Preparation.

The preparation of the normal pyrophosphate is achieved by direct or indirect pyrolysis of disodium hydrogen orthophosphate. Thus, when a salt such as sodium chloride or a sodium base is heated to above 250° with phosphorus pentoxide in the presence of steam[1,2] or with phosphoric acid[3-5] when the sodium:phosphorus ratio is 2:1, or when the secondary orthophosphate is heated alone,[6-8] the normal pyrophosphate results. In the laboratory, the pyrolysis of the secondary orthophosphate is most commonly used[9] (5 hours at 500° C.[10] or less time at 1100° C.[11] is recommended), but reference has been made to the preparation of tetrasodium diphosphate in various other ways:- (*a*) By the action of cyanogen, prepared *in situ* from silver cyanide, on trisodium orthophosphate at 270°:-[12]

$$2Na_3PO_4 + (CN)_2 \rightarrow Na_4P_2O_7 + NaCN + NaCNO.$$

(*b*) By the action of sodium nitrate above 320° C. on a compound believed to be sodium dimetaphosphate:-[13,14]

$$2Na_2P_2O_6 + 4NaNO_3 \rightarrow 2Na_4P_2O_7 + 4NO_2 + O_2.$$

(*c*) By the similar action of sodium halides,[15] especially the iodide,[16] on this metaphosphate at 650° to 750°C., e.g.:-

$$2Na_2P_2O_6 + 4NaI + O_2 \rightarrow 2Na_4P_2O_7 + 2I_2$$

(no phosphites are formed in this reaction, except possibly in the absence of oxygen). (*d*) At a high temperature the same dimetaphosphate acts on trisodium orthophosphate to give the normal pyrophosphate:-[16,17]

$$2Na_3PO_4 + Na_2P_2O_6 \rightarrow 2Na_4P_2O_7.$$

Silica probably acts as a catalyst in these metaphosphate reactions, and mixed pyrophosphates, e.g., $Na_2K_2P_2O_7$ or $Na_2CaP_2O_7$, are formed in analogous reactions with potassium or calcium compounds. (*e*) It has been stated that at 85° to 120° sodium triphosphate hexahydrate decomposes as follows:-[18,19]

$$Na_5P_3O_{10},6H_2O \rightarrow Na_4P_2O_7 + NaH_2PO_4 + 5H_2O,$$

although it has also been suggested that the product may be trisodium hydrogen pyrophosphate mixed with disodium hydrogen orthophosphate.[20,21]

Tetrasodium pyrophosphate decahydrate is prepared by crystallizing the anhydrous salt from water below 79°C.[9]

Separation of the salt from other sodium phosphates has been achieved in the laboratory by means of paper chromatography[22-25] and paper electrophoresis.[26] R_f values are given under Sodium orthophosphates, Table VII (see page 1272).

Uses.

The salt, known in commerce as TSPP, has been of considerable interest as one of the earliest condensed phosphates that found application in water treatment for preventing calcium salt deposition,[8,27-34] in acting as a mild detergent[35-43] or in pH control.[44-46] It is often used in germicidal preparations[47-49] and in mixed soap compositions[8,50-66] where its non-hygroscopic nature is an advantage. Its sequestering properties in solution have also been used in the removal of iron and other contaminating cations,[57,66-72] in descaling recipes[73] and in the dyeing trade.[51] Its ability to prevent flocculation of colloids has been used in dispersing clays,[74-76] alumina[77] and calcium carbonate.[78] Tetrasodium pyrophosphate has been used in preventing the corrosion of steel,[79,80] in stabilizing hydrogen peroxide both in solution[81-83] and as solid per-salts,[8,84,85] in retarding the corrosive action of sodium hydroxide on glass[86] and in improving the throwing power of cupric solutions during electrolysis.[87] Mention has been made of its use as a flotation agent,[88,89] as a partial replacement of borax in glasses[90] and as a thinner in enamels.[91] The salt can be used to depress the swelling of gypsum[92] and to improve the resistance to wear of electrical contact brushes.[93] When fused with sodium metaphosphate in equimolar proportions the salt affords one method of preparing sodium triphosphate (q.v.). TSPP is used in treating[94] and in coating or glazing paper[95-97] and it has found application in stabilizing vinyl polymers,[98-101] presumably owing to its sequestering action on harmful catalytic cations. The salt has been added as a moderator or activator to polymerizing systems[102-110] and in the refining of glyceride fats.[111] In the food industry, sodium pyrophosphate has been used in sausage manufacture,[112] in the preparation of baking powders[113] and in stabilizing fruit juice colours.[114]

Physical Properties.

High temperature microscopy in polarized light, supported by thermal expansion evidence, shows the existence of at least five forms of solid sodium pyrophosphate, type V being the stable form at room temperature:-

$$Na_4P_2O_7\text{-V} \overset{400^\circ}{\rightleftharpoons} Na_4P_2O_7\text{-IV} \overset{510^\circ}{\rightleftharpoons} Na_4P_2O_7\text{-III} \overset{520^\circ}{\rightleftharpoons} Na_4P_2O_7\text{-II} \overset{545^\circ}{\rightleftharpoons} Na_4P_2O_7\text{-I} \overset{985^\circ}{\rightleftharpoons} \text{melt}$$

The changes are all reversible and *X*-ray measurements show that type-V is the species in solution.[115] The crystals at room temperature are biaxial positive, $2V = 40°$, $\alpha = 1·475$, $\beta = 1·477$ and $\gamma = 1·496$ (white light),[115,116] while the decahydrate is also biaxial positive with $2V = 60·5°$, $\alpha = 1·450$, $\beta = 1·4525$ and $\gamma = 1·460$.[117] The anhydrous salt shows an intensity maximum at 4·39A. in its X-ray diffraction pattern;[118] details of the patterns have been published.[115] Infra-red absorption spectral characteristics of anhydrous tetrasodium diphosphate and its decahydrate are given in Table XV.[119]

TABLE XV.- INFRA-RED ABSORPTION BANDS OF TETRASODIUM DIPHOSPHATE

$Na_4P_2O_7$		$Na_4P_2O_7, 10H_2O$	
Wave number ($cm.^{-1}$)	Intensity	Wave number ($cm.^{-1}$)	Intensity
1180	strong, sharp	3420	strong
1165	strong, sharp	3230	strong
1150	very strong	3000	strong
1124	very strong	1655	medium
1031	strong	1110	very strong
988	strong	1093	very strong
921	very strong, broad	1021	weak
895	medium	993	medium
735	very strong	921	strong, broad
		865	medium
		665	medium, very broad

The melting point of the anhydrous salt is given as 985°C.,[115,120] and 980°[121] and of the decahydrate as 79·5°C.[10]

The solubility has been quoted as 4·96% of the anhydrous salt at 60°F. and 28·7% at 212°F.[122] and 7·5g. per 100g. of water at 20°C.[123] Further details are given in Table XVI: these data show the loss of the ten molecules of hydration of the hydrated salt at 79·5 ± 0·5°C.[121]

TABLE XVI.- SOLUBILITY OF TETRASODIUM PYROPHOSPHATE[121]

Temperature (°C.)	Per 1000g. of solution		Per 1000g. of water	
	$Na_4P_2O_7$(g.)	$Na_4P_2O_7$(g.mol.)	$Na_4P_2O_7$(g.)	$Na_4P_2O_7$(g.mol.)
-0·43	21·4	0·080	21·8	0·082
0	21·9	0·082	22·36,[124] 22·4	0·084
18	-	-	51·47[124]	-
20·0	52·2	0·196	55·1	0·207
25	-	-	66·18[124]	-
40·0	98·1	0·369	108·7	0·409
60·0	197·5	0·743	246·4	0·926
76·0	330·4	1·204	471·4	1·772
82·0	351·3	1·320	541·7	2·083
96·0	311·5	1·170	452·5	1·670

The normal salt is insoluble in 98·2% glycerol, but 9·6g. of the salt dissolves in 100g. of 86·5% glycerol at 20°C.[125] Heats of solution in water are: anhydrous salt, +11·85 kg.-cal./mol.; decahydrate, -11·67 kg.-cal./mol.; the heat of hydration is 124·5 kg.-cal./mol.[121] Where h is the reciprocal of concentration, the specific heat of solution, y, is $\frac{69·57 + h}{92·12 + h}$ at 18–20°.[126] The Raman spectrum of solutions of the mixed salt disodium dipotassium pyrophosphate has been investigated.[127]

A 1% aqueous solution of the anhydrous salt has a pH 10·2,[10,122,123] and the pH-electrometric titrations with sodium hydroxide and hydrochloric acid are given in Fig. 7,[128] together with those of other sodium phosphates. Dissociation constants of pyrophosphoric acid (in sodium pyrophosphate-hydrochloric acid mixtures) have been redetermined: k_4 is given as[129] $1{\cdot}32 \times 10^{-10}$ and[11] $2{\cdot}4 \times 10^{-10}$ or[130,131] $3{\cdot}6 \times 10^{-9}$; k_3 as[129,11,130] $1{\cdot}98 \times 10^{-7}$, $2{\cdot}7 \times 10^{-7}$, $7{\cdot}6 \times 10^{-7}$ and $2{\cdot}9 \times 10^{-7}$;[131] k_2 as $1{\cdot}1 \times 10^{-2}$ and k_1 as $1{\cdot}4 \times 10^{-1}$.[131] At 65·5° the figures are:[132] k_4, $9{\cdot}81 \times 10^{-9}$; k_3, $1{\cdot}45 \times 10^{-6}$; k_2, $7{\cdot}58 \times 10^{-3}$; k_1, $1{\cdot}07 \times 10^{-1}$. The most recent data[11,132] embody corrections for the presence of carbon dioxide and for ion association. The dissociation constant of the equilibrium $NaP_2O_7''' \rightleftharpoons P_2O_7'''' + Na^{\bullet}$ has been given as $4{\cdot}5 \times 10^{-3}$.[11] The specific conductivity of the salt in acetic acid and water mixtures shows a break at 35–38°C. which may be due to increased hydration or polymerization which affects the mobility of the ions.[133] At infinite dilution Λ_0 is 146·0, of which 95·9 is attributed to the pyrophosphate anion.[11] The conductivity shows a positive pressure coefficient,[134] greater than that of orthophosphates. At pH 7·8 the salt has a dialysis coefficient of 0·502.[135] R_f values[22,23] in various solvents on filter paper have been given in Table VII (see page 1272).

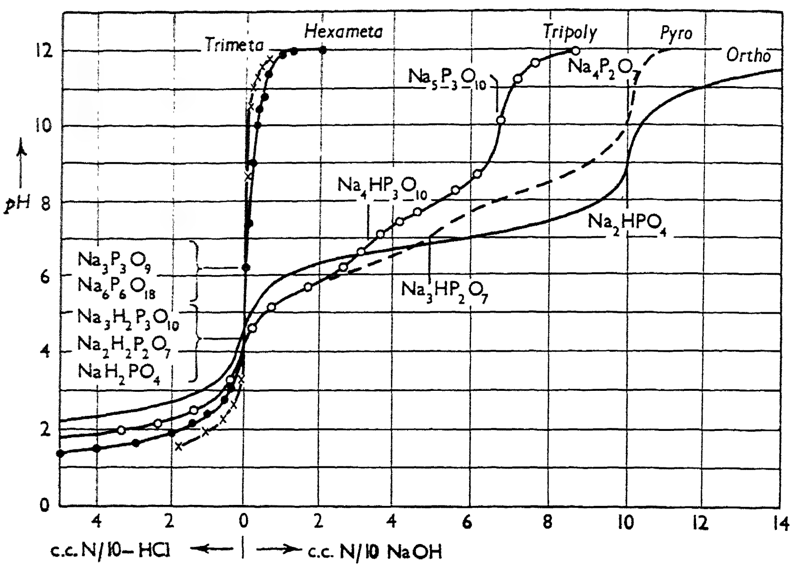


FIG. 7. ELECTROMETRIC TITRATION OF NORMAL SODIUM PHOSPHATES (0·001 PHOSPHORUS EQUIVALENT CONCENTRATION) WITH HYDROCHLORIC ACID AND SODIUM HYDROXIDE

The effect of sodium pyrophosphate on other systems has been examined. Its cryoscopic effect on the freezing point of saturated sodium sulphate solutions containing sulphuric acid[136] and of fused lithium borate[137] has been investigated; the quenching of the fluorescence of quinine by bromide and of fluorescein by iodide in the presence of the salt is a simple salt effect;[138] the mutarotation of glucose is more rapid in solutions containing the salt than in similar solutions of disodium orthophosphate owing to the increased pH;[139]

the electrodeposition of tin from stannous solutions in the presence of sodium pyrophosphate has been studied in detail;[140] silver pyrophosphate is soluble to the extent of 0·0324g. per 100ml. of cold saturated tetrasodium pyrophosphate solution;[141] the swelling of gelatin is inhibited by the salt and the diffusion of methylene blue is increased;[142] the critical concentration for micelle formation in soap solutions is lowered by the salt owing to the common ion effect[143] or other relationships[144] and the transition temperature from crystalline to liquid-crystalline forms of sodium palmitate is markedly affected by the salt;[145] the viscosity of sodium silicate detergents is lowered by the salt;[146] adsorption of sodium alkylbenzenesulphonates and sodium palmitate was reduced in the presence of the salt;[147] positive silver halide sols show a reversal of particle charge in the presence of the salt[148] and the dispersing action of TSPP on 4% suspensions of lead arsenate in water[149] and on clays[150] has been investigated; the salt decreases the particle size of clays in suspension and hence decreases the viscosity[151] and other effects have also been recorded;[75] the ζ-potential of apatite, calcite and dolomite is markedly increased by the normal pyrophosphate thus suppressing their flotation with sodium oleate.[152]

Chemical Properties.

The presence of radioactive orthophosphates, pyrophosphates and phosphites has been demonstrated in the products obtained upon irradiation of anhydrous tetrasodium pyrophosphate and its decahydrate with neutrons.[153] In fused lithium metaborate the anhydrous salt dissociates:-[137]

$$Na_4P_2O_7 \rightleftharpoons 4Na^{\cdot} + PO_4''' + PO_3'$$

The system $Na_4P_2O_7$-$(NaPO_3)_x$ has been examined extensively: at 552°C. there is a eutectic containing 0·31 weight fraction of the pyrophosphate with the metaphosphate and sodium triphosphate as the crystalline phases: the two forms of the triphosphate appear to be the only compounds formed in this system,[115,120] although various claims have been made for the formation of higher polyphosphates. The section of the Na_2O–P_2O_5 diagram bounded by sodium pyro- and meta-phosphates is shown in Fig. 8, which is discussed in greater detail under sodium triphosphate. Heated with trisodium orthophosphate at 250° to 260°, the normal pyrophosphate gives 20% yields of polyphosphate within 30 minutes, as indicated by radio-phosphorus (^{32}P) measurements.[154] Mixtures of phosphorus pentoxide and tetrasodium pyrophosphate when progressively heated are said to yield successively (*a*) an unstable sodium dimetaphosphate; (*b*) insoluble sodium metaphosphate of the Maddrell type; (*c*) a reaction product of (*a*) and (*b*); (*d*) sodium trimetaphosphate and, finally, (*e*) the glassy sodium metaphosphate melt.[155] In the presence of oxygen, sodium iodide and pyrophosphate react as follows:-[16]

$$4NaI + 2Na_4P_2O_7 + O_2 \rightarrow 4Na_3PO_4 + 2I_2.$$

The system $BaSiO_3$–$Na_4P_2O_7$ has been examined and phase equilibrium diagrams published, but no double compounds have been reported;[156] on the other hand the systems sodium pyrophosphate with sodium chromate, molybdate or tungstate respectively show the existence of double compounds: $Na_4P_2O_7,4Na_2CrO_4$, m.p. 916°C., $Na_4P_2O_7,2Na_2MoO_4$, m.p. 821°C. and $Na_4P_2O_7,2Na_2WO_4$, m.p. 767°C. (decomp.), in contrast to the simple eutectics of the analogous potassium series.[157,158] The sodium tungstate system also displays a peritectic at 767°C. containing 42% of sodium pyrophosphate and a eutectic at 647°C. containing 15% of the salt.[159] Barium titanate is soluble in sodium pyrophosphate to the extent of approximately 40% at 1000° to 1100°C., displaying a crystallization curve minimum at 853°C. corresponding to a 13 mole percentage of barium titanate; no true eutectics or double compounds are found owing

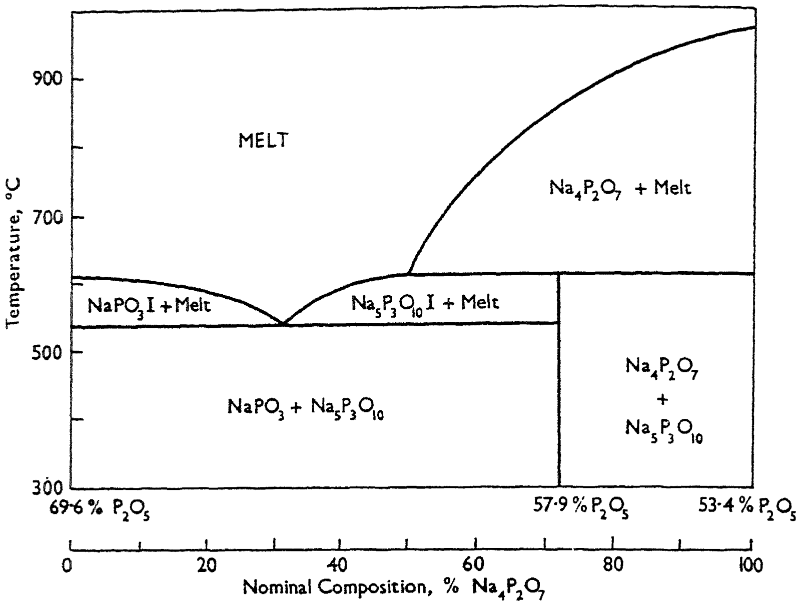


FIG. 8. THE SYSTEM $NaPO_3$-$Na_5P_3O_{10}$-$Na_4P_2O_7$

to the reaction:-[160]

$$2BaTiO_3 + Na_4P_2O_7 \rightleftharpoons Ba_2P_2O_7 + 2Na_2TiO_3.$$

With sodium fluoride a eutectic is formed at 734° C., and the system NaF-$BaTiO_3$-$Na_4P_2O_7$ has been examined in detail.[161] Analogous studies have been made with lead titanate: a minimum (not a eutectic or evidence of binary compounds) is found at 922°C., corresponding to 9 mole-% of lead titanate, in the crystallization curves of the system $PbTiO_3$-$Na_4P_2O_7$, and a double decomposition reaction similar to that of the barium titanate system renders the system unstable.[162]

Hydrolysis of tetrasodium pyrophosphate is of interest intrinsically and also because the compound plays an intermediary role in the hydrolysis of metaphosphates to orthophosphate, especially in alkaline solution. Hydrolysis is accelerated with increasing acidity[163-166] and with increasing temperature.[163,164] Even in 1% aqueous solution hydrolysis is appreciable, especially at temperatures near the boiling point,[167-172] but in an excess of sodium hydroxide at 100°C. for 96 hours the pyrophosphate anion is unchanged:[171] the decrease of rate of hydrolysis with increasing pH and decreasing temperature is very abrupt.[169,171,172] Kinetic data for aqueous hydrolysis at 100°C. of the sodium pyrophosphates are given in Table XVII.

In the range 30° to 90°C. and 0·350 to 0·500M. solutions of hydrochloric acid, hydrolysis rates of 0·125M. pyrophosphate solutions may be represented by the expression:-

$$kt = -102{\cdot}860\log X - 68{\cdot}143 + 109{\cdot}590X - 42{\cdot}598X^2,$$

where X is the fraction of unchanged pyrophosphate. Temperature coefficients of 3·4 at 75°-90°C. at 0·500M. and 7·0 at 30°-45°C. at 0·350M. hydrochloric acid are extremes of this series.[173] A general expression:-

$$-\frac{dc}{dt} = k_0[P_2O_7''''] + k_1[HP_2O_7'''] + k_2[H_2P_2O_7''] + k_3[H_3P_2O_7'] + k_4[H_4P_2O_7]$$

TABLE XVII.- HYDROLYSIS RATE CONSTANTS OF THE PYROPHOSPHATES AT 100°C.

Compound	pH	Rate constant (sec.$^{-1}$)	Half life (min.)
$H_4P_2O_7$	1·92	$8{\cdot}3 \times 10^{-4}$	14·5[169]
$NaH_3P_2O_7$	2·07	$2{\cdot}4 \times 10^{-4}$	47·5[169]
$Na_2H_2P_2O_7$	3·21	$1{\cdot}44 \times 10^{-4}$	80·0[169]
$Na_3HP_2O_7$	7·34	$7{\cdot}8 \times 10^{-5}$	198·5[169]
$Na_4P_2O_7$	9·33	$1{\cdot}7 \times 10^{-6}$	- [171]

has been proposed, on the assumption that each species hydrolyses at a rate depending on its concentration and that hydrogen ion concentration serves only to determine the proportion of each species.[132] At 37°C., 80, 67, 5·4 and 0·6% of the salt are hydrolyzed within 30 minutes in, respectively, 5·7, 5·0, 0·8 and 0·1N. solutions of hydrochloric acid.[174] The presence of magnesium has no appreciable effect on the hydrolysis,[174,175] but calcium,[175] lanthanum and aluminium ions tend to increase the rate.[174]

It hot water the hydrolytic reaction is:-[163,171]

$$Na_4P_2O_7 + H_2O \rightarrow 2Na_2HPO_4,$$

but there is some evidence for an intermediate unstable species between the pyro- and ortho-phosphate in acetic acid solution.[133]

Pyrophosphatase hydrolysis of the pyrophosphate at pH 7·3 produces an enthalpy change of 5810 g.-cal./mol., and this figure is due solely to the pyro- to ortho-phosphate conversion; the reaction is of zero order as far as 80% of completion, with a maximum specific rate constant of $2{\cdot}77 \times 10^{-7}$ moles/litres-sec. per μg. of enzyme/ml.[176] Whereas in the above experiment magnesium ions are said to have no influence on the reaction, it has been stated that these ions have an activating effect owing to the complex ion MgP_2O_7'' which is the enzymic substrate.[177]

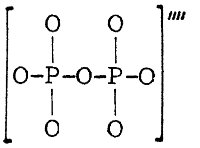
The system $Na_4P_2O_7$–$AgNO_3$–H_2O shows a tyndallometric maximum which is dependent on concentrations of silver nitrate and nitric acid.[148] Sodium pyrophosphate in contact with gelatin soaked in silver nitrate gives rise to zones of different densities of precipitation differing from the normal type of Liesegang rings obtained, for example, with orthophosphate.[142] Cupric solutions impregnated into gelatin give a series of rings with pyrophosphate, the spacing of the rings decreasing with increasing distance from the central mixing point.[178] Solid calcium carbonate is said to undergo no reaction with solutions of sodium pyrophosphate.[179] Pyrophosphate is quantitatively precipitated from a solution of its sodium salt at pH 3·8 to 3·9 with zinc acetate, and the resulting zinc pyrophosphate can be titrated compleximetrically.[180] The products of the reactions of tetrasodium diphosphate with hexamminecobaltic chloride and with *p*-phenylenediamine hydrochloride have been examined microscopically and described for analytical purposes.[181] It has been observed that a slight excess of the pyrophosphate, applied as its normal sodium salt, forms non-ionized complexes with magnesium, iron, aluminium, zinc, manganese, chromium, copper, nickel, barium, strontium and certain other ions, but precipitates only with lead, silver and mercuric ions.[122] But at pH 4·1 in the presence of a little acetone, the pyrophosphate is quantitatively precipitated with manganous ions and, after separation of polymetaphosphates as their insoluble barium salts, this reaction forms the basis of a precise method of determining pyrophosphate and effecting its separation from other phosphates.[182] The sequestering action of pyrophosphate on calcium ions is of particular importance in the treatment of hard waters: whilst its efficiency of action is said to decrease in high concentrations of the salt,[32] it is effective in preventing precipitation of calcium carbonate from aqueous solutions at a concentration as low as 2 p.p.m. In order to prevent precipitation of calcium carbonate from a 100 p.p.m. solution, 800 p.p.m. of tetrasodium pyrophosphate are required (cf. 417 and 306 p.p.m. for triphosphate and polymetaphosphate glass respectively[123]). This sequestering ability is probably due to the geometry of the O–P–O–P–O chain which is favourable to adsorption on the growing calcite lattice, thus preventing further crystallization.[30] Polarographic investigation indicates that a similar removal of barium ions from solution is due to precipitation of barium pyrophosphate.[28] Analogous sequestering or precipitation reactions occur with iron, magnesium and certain other cations, and some insoluble phosphates dissolve in solutions of tetrasodium diphosphate.[8] Addition of cupric ions to aqueous sodium pyrophosphate leads to the successive formation of the compounds $Na_6Cu(P_2O_7)_2$, $Na_2Cu_3(P_2O_7)_2$ and $Cu_2P_2O_7$.[183] Polarization of cathodes upon which copper is being deposited from aqueous solutions containing sodium pyrophosphate is shown to increase with increasing concentration of the salt, but to decrease with increasing temperature, in accord with a hypothesis of complex formation: the slow process in the deposition is not the decomposition of this complex ion but is probably concentration polarization due to slow diffusion, the activation energy of which is 4·5 kg.-cal. in a solution of 0·1M. cupric sulphate containing 0·2M. sodium pyrophosphate.[184] In very low concentrations of sodium pyrophosphate the polarization is due to precipitation of cupric pyrophosphate, but formation of the soluble salt $Na_2CuP_2O_7$ occurs at higher pyrophosphate concentrations.[185] Similarly, at the anode, copper dissolves at low current density into sodium diphosphate solutions forming complex copper pyrophosphates, but at higher current density a brown, non-passivating oxide deposits on the anode; when oxygen evolution becomes competitive, cupric pyrophosphate deposits owing to local insufficiency of soluble pyrophosphate concentration. The limiting current density is raised by normal techniques used for reducing passivation. Zinc also forms its insoluble normal pyrophosphate at high current density.[186] The sequestering of iron with sodium pyrophosphate has been of use in removing such impurities.[99-101] The following sparingly soluble double salts have been prepared: $Na_4P_2O_7,3Mg_2P_2O_7,21H_2O$, $7Na_4P_2O_7,25Mg_2P_2O_7,172H_2O$, $2Na_4P_2O_7,2Zn_2P_2O_7,5H_2O$, $3Na_4P_2O_7,9Zn_2P_2O_7,16H_2O$, $8Na_4P_2O_7,7Zn_2P_2O_7,23H_2O$, $Na_4P_2O_7,4Cu_2P_2O_7,17H_2O$, $8Na_4P_2O_7,7Cu_2P_2O_7,13H_2O$, $Na_4P_2O_7,Mn_2P_2O_7,8H_2O$, $Na_4P_2O_7,3Co_2P_2O_7,20H_2O$, $3Na_4P_2O_7,9Co_2P_2O_7,20H_2O$, $Na_4P_2O_7,Ni_2P_2O_7,12H_2O$. In the same investigation, only the soluble $3Na_4P_2O_7,Cu_2P_2O_7,32H_2O$ showed true complex formation with copper in the anion.[187]

Equilibria in the system $Na_4P_2O_7$–H_2O–H_2O_2 have been studied.[188] Addition of hydrogen peroxide to a solution of tetrasodium diphosphate increases the solubility of the salt owing to double compound formation. A compound $Na_4P_2O_7,3H_2O_2$ is stable at 70°C. in a vacuum but decomposes completely at 130°C., and the hydrogen peroxide is readily removed by extracting with ether.[124] The binding of the peroxide, as hydrogen peroxide of crystallization, is stronger than that in the analogous orthophosphate compounds[189] and comparable with the urea-hydrogen peroxide compounds.[85] The salt acts as a stabilizer for hydrogen peroxide solutions in which it permanently decreases the rate of decomposition rather than acting as a temporary but complete inhibitor:[82] this action may be due to the sequestering of catalytic iron as $[Fe(OH)_2P_2O_7]''$ or $[Fe(OH)_2P_2O_7]'''$.[83] Excessive concentrations of sodium pyrophosphate, however, promote decomposition.[83,190]

The salt does not undergo the molybdenum blue reaction.[191] Corrosion of enamels by sodium pyrophosphate has been examined,[192,193] and the marked attack on magnesium–aluminium alloys has been ascribed to the sequestering action of the salt on the metals present.[194]

Tetraethyl pyrophosphate, an insecticide, is prepared by heating tetrasodium pyrophosphate (1 mol.) with excess (4 mols.) of ethyl iodide or diethyl sulphate in acetone solution.[195]

Tetrasodium diphosphate can be determined acidimetrically in simple solutions, using dimethyl yellow as indicator.[130] In the presence of not more than a nine-fold excess of triphosphate the gravimetric zinc pyrophosphate method, employing an extended digestion time and double precipitation, is recommended;[10,191,196] orthophosphate and up to a twenty-fold excess of glassy polymetaphosphates do not interfere.[191,196] If triphosphate is absent a direct pH-electrometric method can be employed.[191,197] It has been stated that highly accurate and precise methods for determination of the range 4 to 10% in complex phosphate mixtures are not available.[198] Aqueous analytical methods have been reviewed.[198,199] An isotope dilution method, using ^{32}P, has been described for the determination of pyro- and tri-phosphates occurring together.[200] In similar mixtures, *X*-radiography, for example using microphotometry,[19] employing magnesia as an internal standard[201] or by extrapolation of the intensity of the 4·39A. band after addition of successive known quantities of the pyrophosphate has been successfully employed.[118] Characteristics of the decahydrate under the microscope have been described for identification purposes.[163] The basic structure of the pyrophosphate ion is accepted as:-



$$\left[\mathrm{O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{P}}{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{P}}{-}O}\right]^{''''}$$

in the light of its known chemical properties and its position as second member of the series $Na_{n+2}P_nO_{3n+1}$.

Trisodium Hydrogen Pyrophosphate

This salt, the preparation of which was in doubt for some time, can be prepared by evaporating a mixture of solutions of disodium hydrogen orthophosphate and tetrasodium pyrophosphate in the ratio 10:13·5. The dry product is either the tetrahydrate or, if the evaporation is carried out slowly, the pentahydrate.[202] The mono- and nona-hydrates can be prepared by treating disodium dihydrogen pyrophosphate with sodium hydroxide followed by evaporation and crystallization.[203] The hexa- and hepta-hydrates, and possibly the decahydrate, have been described and may crystallize from solutions of the salt between 20° and 30°C.[163] It has been pointed out[163] that the ease with which the tetrasodium pyrophosphate decahydrate forms metastable solutions within the system $NaOH{-}H_4P_2O_7{-}H_2O$ can readily obscure the formation of the trisodium salts, which, in any case, occupy only a small section of the equilibrium diagram. The more hydrous salts are successively converted into less hydrated salts with increase of temperature, the last molecule of water being lost at 180°[202] or 150°.[203]

The anhydrous salt is believed to be a constituent of the mixture obtained on heating sodium triphosphate hexahydrate at 120°[20] and its monohydrate is found in the mixture obtained on keeping the same polyphosphate for 2·5 years in a stoppered bottle.[21] The equation:-

$$32Na_5P_3O_{10},6H_2O \rightarrow 13Na_4P_2O_7 + 26Na_3HP_2O_7 + 10NaH_2PO_4 + 8Na_2HPO_4 + [166H_2O]$$

is said to give an approximate description of these reactions.[163] Heating sodium ammonium hydrogen orthophosphate leads to the formation of the tertiary salt disodium ammonium hydrogen pyrophosphate at 220° C.[204]

The salt finds application, in a synergistic capacity, in detergent compositions.[8]

Solubility data are recorded in Table XVIII.[203] The transition point between the nona- and mono-hydrates is 29•6°.

TABLE XVIII. - SOLUBILITY OF TRISODIUM HYDROGEN PYROPHOSPHATE

Temperature (°C.)	Solubility (%)	
	$Na_3HP_2O_7,9H_2O$	$Na_3HP_2O_7,H_2O$
20•7	14•15	–
26•5	20•00	–
29•0	22•62	–
32•9	27•50	22•15
36•1	32•70	21•55
42•2	–	20•30
49•5	–	18•90

The third dissociation constant of pyrophosphoric acid has been given as ($\times 10^{-7}$) 2•7,[11] 1•98,[129] 7•6,[130] and 14•5.[132]

At 300°C. the salt is said to yield sodium tetraphosphate, $Na_6P_4O_{13}$,[202] but this is doubtful.[8,11,205] At 500° a mixture of triphosphate and trimetaphosphate is produced:-[8,203]

$$6Na_3HP_2O_7 \rightarrow 3Na_5P_3O_{10} + (NaPO_3)_3 + 3H_2O.$$

During pyrolysis of sodium triphosphate hexahydrate the products obtained at 120°, which include the tertiary pyrophosphate, recombine at higher temperatures to give anhydrous sodium triphosphate,[20] rather than react intramolecularly, owing to the suitable disposition of the ions in the mixture.

The salt is more stable as a 1% aqueous solution than the corresponding solution of the normal salt.[8] Rate constants are given in Table XVII.[169,171] In aqueous solution the products are disodium hydrogen orthophosphate and sodium dihydrogen orthophosphate.[163] Sequestration properties similar to those of the normal salt have been observed and applied.[8]

Disodium Dihydrogen Pyrophosphate, Disodium Dihydrogen Diphosphate

Preparation.

The most common method of preparing the secondary salt of pyrophosphoric acid is by thermal dehydration, sometimes under vacuum, of sodium dihydrogen orthophosphate (or the correct proportions of phosphoric acid with sodium hydroxide, chloride or carbonate) at temperatures above 150°C., although the reaction does not become appreciable until approximately 180° to 200°C. is reached:-[8,10,18,204,206-212]

$$2NaH_2PO_4 \rightarrow Na_2H_2P_2O_7 + H_2O.$$

At temperatures higher than 225° the product begins to lose 'molecular' water with formation of the metaphosphate series.[20,204,212] The pressure equilibrium data for the system have already been given in Table XIV (see page 1280). By carrying out the decomposition of the primary orthophosphate in a moist atmosphere, the temperature can be raised without formation of the metaphosphates.[213,214] Alternatively, the salt may be prepared by addition of calculated quantities of hydrochloric,[215,216] sulphuric,[217] acetic[10] or phosphoric[218] acids to an aqueous solution of tetrasodium pyrophosphate: the acid salt is salted out, for example, with sodium chloride. Reference has been made to the controlled hydrolysis of sodium metaphosphate (especially glassy polymetaphosphates and sodium trimetaphosphate) at 170° to 300°C. by means of steam, possibly under pressure.[219] The storage quality of the acid salt can be improved by adding traces of potassium and aluminium phosphates[214] or by physical treatment.[220,221]

The hexahydrate, $\mathrm{Na_2H_2P_2O_7,6H_2O}$, is obtained on crystallizing the salt from cold water,[10,222] but dehydration is complete below 100°C. and probably at 36°.[10]

Complex diarsenatophosphates, $\mathrm{Na_2H_2(P,As)_2O_7}$ and $\mathrm{Na_4(P,As)_2O_7}$, are prepared by heating mixed disodium hydrogen orthoarsenatophosphates, $\mathrm{Na_2H(P,As)O_4}$, containing an As:P ratio of $\geqslant 1:1$.[223]

Uses.

One of the main uses of disodium dihydrogen diphosphate lies in its intermediary role in the manufacture of the sodium metaphosphates. It has, however, been used also in the preparation of baking powders,[220,221,224] for improving cheese,[225] in stabilizing fish extracts[226] and in the treatment of fabrics before dyeing.[8]

Properties.

The following optical properties have been given: anhydrous salt (as fine needles with positive elongation) biaxial negative, $\alpha' = 1{\cdot}510$, $\gamma' = 1{\cdot}517$;[10,117] (as orthorhombic pyramidal crystals) α 1·501, β 1·514, γ 1·522;[10] hexahydrate, biaxial negative, $2V$ 32°, $\alpha = 1{\cdot}460$, $\beta = 1{\cdot}4645$, $\gamma = 1{\cdot}465$.[10,116] Infra-red absorption characteristics are given in Table XIX.[119] In the Raman spectrum, the displacement, $\Delta\nu$, is given as 1105 $\mathrm{cm.^{-1}}$ with the 4358A. mercury line irradiation.[127] The effect of the salt on the ζ-potentials of several solids has been examined.[227] Solubilities in the closed tube at high temperatures have been reported.[228] The pH of a 1% aqueous solution is[8] 4·6 or 4·1 to 4·3.[10]

The action of heat on disodium dihydrogen pyrophosphate has proved of interest: the hexahydrate rapidly loses water at relatively low temperatures (36°) and the loss is complete by 100°C.[10,222] (some hydrolysis to orthophosphate may occur during this heating[163]) and upon heating the residue of anhydrous salt in a dry atmosphere or under vacuum 'molecular' water is lost, beginning at approximately 220° to 225°, with direct formation of sodium metaphosphates without any known intermediates. The rate of loss is appreciable at 240° to 250°[164,229] and rapid at 265° to 270°C. When heated over the temperature range 250° to 628°C., a sequence of mixtures of various sodium metaphosphates is formed (sodium metaphosphate-III, -II, -I and glass, q.v.).[164,229] It has been claimed that the moisture content of the ambient atmosphere has a considerable effect on the products: thus, at 305°C. in moist air a soluble metaphosphate and at 330°C. in dry air an insoluble sodium metaphosphate predominate.[168] Dissociation pressures of the reaction (closed system):-

$$x\mathrm{Na_2H_2P_2O_7} \rightleftharpoons 2(\mathrm{NaPO_3})_x + x\mathrm{H_2O}$$

are presented in Table XX.[206]

Hydrolysis of the salt in aqueous solution leads to two molecules of sodium dihydrogen orthophosphate,[163] requiring 30 minutes for half conversion in N/16 solutions at 55° to 100°C.[230] Other data are presented in Table XVII.[169,171] Although hydrolysis is rapid at 100°C. in a 1% solution, at 70° no change was observed after 25 hours:[8] this is contradicted in that 10% has been said to be hydrolyzed (reverted) at 70° within 6 hours and reversion is complete at 100° in less time.[10]

The normal method of determination of the salt in simple contexts is alkalimetrically following the reaction of a zinc salt with a solution of the acid pyrophosphate:[191,197,231]

$$\mathrm{H_2P_2O_7''} + 2\mathrm{Zn^{\bullet\bullet}} \rightarrow \mathrm{Zn_2P_2O_7} + 2\mathrm{H^{\bullet}}$$

TABLE XIX.- INFRA-RED ABSORPTION BANDS OF DISODIUM DIHYDROGEN DIPHOSPHATE

Wave number (cm.$^{-1}$)	Intensity
~2700	weak, broad
1600	medium, very broad
1389	weak
1333	weak
1210	medium
1191	strong, sharp
1155	strong
1027	weak
957	medium
878	strong, broad
729	medium

TABLE XX. - DISSOCIATION PRESSURES OF THE REACTION
$x\mathrm{Na_2H_2P_2O_7} \rightleftharpoons 2(\mathrm{NaPO_3})_x + x\mathrm{H_2O}$

Temperature (°C.)	Pressure (mm.)
170	10·6
180	34·5
190	59·0
200	84·9
210	115·0
220	154·0
230	208·2
240	289·0
250	411·6
260	526·5
270	650·0
275	717·4
280	760·0

Sodium Trihydrogen Pyrophosphate, Sodium Trihydrogen Diphosphate

Reference has been made to the existence of the trihydrogen pyrophosphate anion, $H_3P_2O_7'$, at pH 2·07 in solutions of sodium hydroxide with pyrophosphoric acid and to the first dissociation constant of the acid (k_1,[131] 1·4 and[132] $1{\cdot}07 \times 10^{-1}$), but no mention has been made of the isolation of solid sodium trihydrogen pyrophosphate.

Sodium Triphosphate, Sodium Tripolyphosphate

Pentasodium Triphosphate, Normal Sodium Tripolyphosphate

Preparation.

In principle, the fusion of mixtures that provide a ratio of sodium to phosphorus of 5:3 with simultaneous adjustment of oxygen ratio should provide a method of preparing the normal triphosphate of sodium. In practice, the conditions of preparation must be rather carefully controlled owing to the ready separation of solid sodium meta- and pyro-phosphates from melts corresponding to a sodium triphosphate composition; moreover, the triphosphate exists in two distinct crystalline forms. Undoubtedly, many of the industrial preparations claimed to contain triphosphate in fact contain, at best, only a small proportion of this condensed phosphate and, in such cases where water softening properties are claimed for the preparation, a polymeric sodium

Refs. p. 1311

metaphosphate is probably the active ingredient. The picture is even more obscure owing to confusions in nomenclature since polymeric metaphosphates, $(NaPO_3)_x$, are sometimes referred to as 'polyphosphates' – a term which should be confined to the series $Na_{n+2}P_nO_{3n+1}$.

The correct sodium–phosphorus balance can be achieved by mixing correct proportions of:-

(*a*) disodium hydrogen with sodium dihydrogen orthophosphate either in the solid state or in solution: the solutions are flash-dried at 350°–450°C.[232-234] and the solids are either heated to 300°–400°C. (*i.e.*, below the melting point, thus giving type-II)[235-237] or are melted and cooled ('tempered') very slowly,[8,10,19,115,120,163,164,182,238-242] which produces type-I which is slowly converted into type-II:

$$2Na_2HPO_4 + NaH_2PO_4 \rightarrow Na_5P_3O_{10} + 2H_2O \quad \xrightarrow[450^\circ C.]{cool} Na_5P_3O_{10}\text{-II}.$$

The importance of catalytic traces of water, which facilitate ionic diffusion, favour the hydrolysis of phosphorus–oxygen–phosphorus linkages and assist crystallization of the product well below the true fusion point, has been discussed:[243] moreover, the required temperature of reaction may be substantially lowered (by as much as 200–250°C.) by adding nitrogenous catalysts such as nitric acid, sodium nitrate or nitrogen oxides;[244]

(*b*) phosphoric acid with disodium orthophosphate,[235,237] sodium hydroxide,[2,235,237] sodium carbonate,[2,5,235-237] or trisodium orthophosphate (or its double salt with sodium fluoride) and sodium hydroxide.[236,242] The mixtures are heated under similar conditions to those in (*a*), e.g., $6H_3PO_4 + 5Na_2CO_3 \rightarrow 2Na_5P_3O_{10} + 3CO_2 + 6H_2O$;

(*c*) phosphorus pentoxide with disodium orthophosphate, sodium hydroxide or sodium carbonate[235,237] again heated under similar conditions, e.g.:-

$$3P_2O_5 + 10NaOH \rightarrow 2Na_5P_3O_{10} + 5H_2O;$$

(*d*) sodium pyrophosphate with sodium trimetaphosphate[9] or polymetaphosphates[19,115,120,163,164,245-248] heated under conditions similar to those described in (*a*):-

$$xNa_4P_2O_7 + (NaPO_3)_x \rightarrow xNa_5P_3O_{10}.$$

Sodium dihydrogen and trisodium orthophosphates undergo similar reactions with sodium metaphosphate at 250°–260°C.[154,245] The sodium pyro-–sodium ortho-phosphate reaction has been examined by a radiotracer technique; after only 30 minutes, at 250°–260°C., a 20% yield of the triphosphate is obtained.[154]

Probably the best method, particularly in the laboratory, involves the hydrolysis of sodium trimetaphosphate at moderate temperatures with sodium hydroxide:-[164,171,249-251]

$$(NaPO_3)_3 + 2NaOH \rightarrow Na_5P_3O_{10} + H_2O$$

Similarly, on heating sodium trimetaphosphate monohydrate to 100°–120°, hydrolysis occurs with formation of sodium triphosphate together with some pyro- and ortho-phosphates.[251]

The hexahydrate, $Na_5P_3O_{10},6H_2O$, is prepared by prolonged exposure of the anhydrous salt to the atmosphere[201] or by crystallizing the salt from cold water,[9,164] especially if followed by salting out with sodium chloride[10] or precipitation with ethanol.[21 245] The hexahydrate is the product of reaction of sodium hydroxide and sodium trimetaphosphate if the reaction mixture is allowed to crystallize over several hours.[249,250] There is some inconclusive evidence for an octahydrate which may be obtained on vacuum evaporation of aqueous solutions of the anhydrous salt at room temperature.[9,205]

The commercial products are rarely purified, and it has been pointed out that aqueous recrystallization must lead to some hydrolysis to sodium pyrophosphate[21] so that purity greater than·99% is rare. In the laboratory, small scale separations from other sodium phosphates have been achieved by paper chromatography[21,22,24,25] or electrophoresis:[26] R_f values are given in Table VII.

Triarsenatophosphates of sodium, $Na_5(As,P)_3O_{10}$, have been prepared by heating to above 192°C. sodium hydrogen orthoarsenatophosphates, e.g., $NaH_2(As,P)O_4$, containing an arsenic to phosphorus ratio of $\geqslant 2:1$.[223] The deepening of colour observed on adding small quantities of sodium carbonate to molten glass polymetaphosphates containing traces of transition elements has been ascribed to polyphosphate formation.[252] Heating disodium alkyl orthophosphates leads to sodium triphosphate mixed with sodium trimetaphosphate at 400°C.[205] The salt hexahydrate was found, mixed with sodium pyro- and meta-phosphates, after neutralization of a 'phosphoric acid' containing 79·8% of phosphorus pentoxide.[253]

Uses.

The primary use of sodium triphosphate lies in its incorporation in detergent compositions and in water softening,[8,33,42,53,56,65,66,163,164,236-238,247,250,254,267] sometimes with germicidal applications.[268] The type-II is undoubtedly preferred in these compositions since type-I tends to form in water a cement-like mass which is difficult to handle.[19] One great advantage of the salt is that, because of its high pH in water (approximately 9·7 in a 1% solution), it does not cause curding of fatty acid soaps.[33,247] Its use in these compositions is mainly due to its ability to sequester especially calcium ions,[32,246,247] and this property is applied directly in preventing the deposition of scale in boilers,[8,236,269] of redeposition of soil[270] and precipitation of gypsum, especially in the cyanidation of gold.[31,271] Similar sequestering properties for other ions are applied, for example, in the removal of iron from leather,[272] wine[273] and glues.[71] Shale used in cement manufacture[274] or clay used in sheeting material[95] can be deflocculated by the salt, and, similarly, the viscosity of drilling muds is markedly reduced.[8,275] The salt has been examined and used as a corrosion inhibitor[8,79,276,277] and in the preparation of oxidation-resistant carbon or graphite compositions.[278] Sodium triphosphate has been used in the refining of glyceride fats[111] and has been incorporated into certain cheeses.[8]

Physical Properties.

The two different crystalline forms of sodium triphosphate caused some confusion during the early history of the salt, and their existence may well explain the supposed formation of 'polymeric' forms of the compound.[115,120,279] Type-I is the stable form above 450°C., the transition point, and type-II is the stable form below this temperature: if type-II is held at a temperature above 450° but below 550°C. it fairly rapidly changes into type-I, but the reverse change, as might be expected at the lower temperature required, is too slow to be economic. Commercially, the preparation must be designed to produce type-II, or the salt must be converted into the hexahydrate, one form only of which exists, and this is then dehydrated below, but near, 450°C.

If melts of the composition $5Na_2O,3P_2O_5$ are cooled from 1000°C., it is clear from the equilibrium diagram (Fig. 8[19]) that at approximately 860°C. tetrasodium pyrophosphate crystals begin to separate from a melt relatively rich in phosphorus pentoxide, but at 622°C., the peritectic point, solid sodium triphosphate begins to appear and, if the melt is cooled slowly enough to maintain equilibrium, virtually all the solid pyrophosphate plus the melt is converted into the triphosphate type-I by 450°C.[115,120,240] On further cooling to approximately 200°C. the crystalline mass frequently spontaneously disintegrates into a fine powder which may be due to formation of small quantities of type-II. The slow rate of the type-I → type-II transformation has been ascribed to the low probability of spontaneous nucleus formation, coupled with the lower temperatures required.[164] Rapid chilling of the melt leads to a glassy material consisting of mixed sodium pyrophosphates and polymetaphosphates.[163] There is no evidence for the presence of higher polyphosphates, such as tetra- and septa-phosphates, in the cooled samples[115,120] although this does not completely exclude the possibility of such compounds which may be stable in the melt at higher temperatures.[163]

Since the anion obtained from both types is identical in solution, investigation of the characteristics of the two types has been mainly by *X*-ray techniques.[19,21,115,246,280,281] The two types can readily be differentiated by the *X*-ray powder method, and by microphotometry of the pattern it is possible to determine sodium triphosphate-I with a precision of ±2% and admixed tetrasodium pyrophosphate with a precision of ±0·5%.[19,118,201] Microphotometer traces for the three mentioned sodium phosphates are given in Fig. 9. Both types belong to space group *C*2/*c* or, possibly, *Cc*, and are monoclinic with the following crystallographic data: type-I, $a = 9{\cdot}73$, $b = 5{\cdot}41$, $c = 19{\cdot}97$ A., β 112° 12′; type-II, $a = 16{\cdot}08$, $b = 5{\cdot}24$, $c = 11{\cdot}28$ A., β 93° 30′.[281] There is a band at 4·57 A.[118] Empirically, the types can be determined in a mixture by a temperature rise test.[282] The hexahydrate, the molecular weight of which has been confirmed as 368 + 6 × 18,[205] has a unit cell containing two molecules of the salt[283] and with $a' = 7{\cdot}53$, $b' = 10{\cdot}23$ and $c' = 9{\cdot}83$.[205,283]

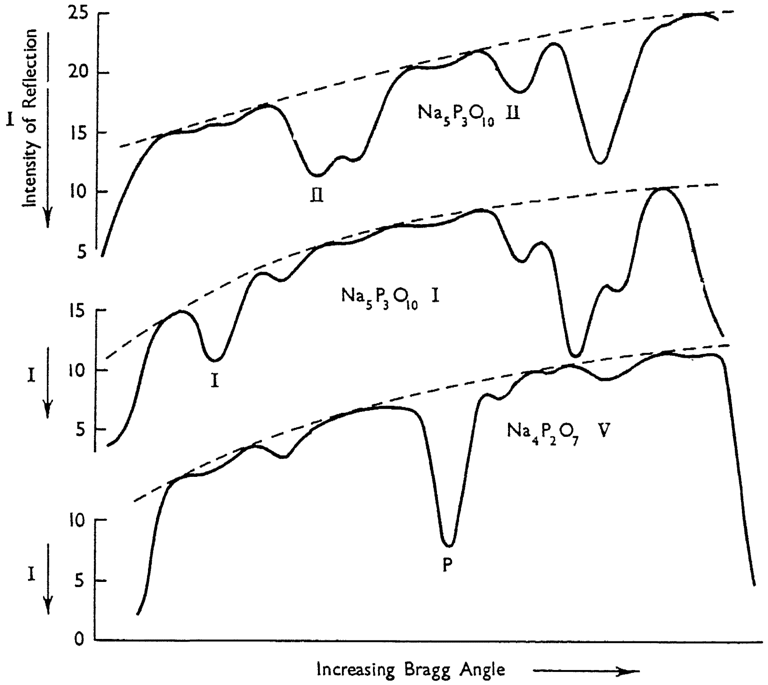


FIG. 9. MICROPHOTOMETER GRAPHS OF $Na_5P_3O_{10}$-II, $Na_5P_3O_{10}$-I AND $Na_4P_2O_7$

Sodium triphosphate hexahydrate forms flat rectangular plates with oblique extinction of 8°–9°; the crystals are often twinned with an extinction at 8° to 9° to the twinning plane.[163] The hydrate and two types of anhydrous salt are biaxial positive; refractive index data are presented in Table XXI.[10,115,116,163,283]

The glass has a refractive index of 1·4814.[115] Infra-red absorption properties of the three sodium triphosphates are given in Table XXII.[119] The densities of type-I, type-II and the hexahydrate are respectively, 2·52, 2·59,[281] and 2·12.[205,283] The incongruent melting point of the anhydrous salt has been

TABLE XXI. - OPTICAL DATA FOR THE SODIUM TRIPHOSPHATES

Salt	2V(°)	α	β	γ	α'	γ'
Type-I	21	1·477	1·478	1·504	1·471	1·500
Type-II	57	1·470	1·477	1·502	1·471	1·500
Hexahydrate	20	1·449	1·450	1·482	1·450	1·470

given as 630°C.[205] or 622°C.,[115,120] and on melting, the salt gives crystals of sodium pyrophosphate accompanied by a liquid containing 0·495 weight fraction of the normal pyrophosphate. The melting point is remarkably sharp.

TABLE XXII.- INFRA-RED ABSORPTION BANDS OF SODIUM TRIPHOSPHATE

$Na_5P_3O_{10}$-I		$Na_5P_3O_{10}$-II		$Na_5P_3O_{10}, 6H_2O$	
Wave number (cm.$^{-1}$)	Intensity	Wave number (cm.$^{-1}$)	Intensity	Wave number (cm.$^{-1}$)	Intensity
~1620	weak, very broad	1214	strong	3630	strong, sharp
1265	weak	1184	strong	3350	medium
1215	strong	1165	very strong	3260	medium
1146	very strong	1145	very strong	1651	weak
1095	strong	1098	strong	1610	weak
1022	weak	1016	weak	1410	weak
989	weak	906	very strong, broad	1211	strong
912	strong, broad	737	medium	1157	strong
798	very weak, broad	665	strong	1118	strong
753	medium			1100	strong
731	weak			1080	strong
708	strong			959	weak
				887	very strong, broad
				768	weak, broad
				710	medium

The salt is not hygroscopic but is readily soluble in water. The solubility given for the commercial material is 17g./100g. of water with a fairly linear temperature relationship[8] at 15°C. and 15·0g./100g. of water at 18°C.[123] Greater detail for a laboratory specimen of 98–99% purity is given in Table XXIII.[21] The flow birefringence of sodium triphosphate mixed with potassium Kurrol salt (a potassium linear polymetaphosphate) in 0·2M. aqueous sodium pyrophosphate has been examined.[284] Heats of solution for types I and II are, respectively, –16·1 and –14·0 kg.-cal./mole,[282] and for the octa- and hexahydrates respectively, –5·76 and –2·78 kg.-cal./mole.[205]

Conductivity data have been examined critically and allowance has been made for hydrolysis: results are in accord with a 1:5-valent type electrolyte.[248] Some data are given in Table XXIV.[205,248]

The ionic mobility of the triphosphate anion is given as 109.[248] Conductivity has a positive pressure coefficient.[134] The dissociation constant of the ionization $NaP_3O_{10}'''' \rightleftharpoons P_3O_{10}''''' + Na^{\cdot}$ is 0·003.[248] The pH of a 1% solution in water at 20° to 25°C. has been variously given as 8·5,[8] 9·4,[191] 9·7,[10] or 9·8.[123,267] pH titrations with N/10 hydrochloric acid and sodium hydroxide have been carried out with a view to elucidation of structure; data, together with those of other sodium phosphates are given in Fig. 7.[128] They show in

TABLE XXIII. - SOLUBILITY OF SODIUM TRIPHOSPHATE

Temperature (°C.)	Solubility (steady state, weight %)	Solid phase
-1•41	13•92	ice
-1•08	8•91	ice
-0•45	3•03	ice
0•00	13•98	$Na_5P_3O_{10},6H_2O$
9•04	13•00	$Na_5P_3O_{10},6H_2O$
20•10	12•92	$Na_5P_3O_{10},6H_2O$
30•00	13•06	$Na_5P_3O_{10},6H_2O$
40•06	13•68	$Na_5P_3O_{10},6H_2O$
50•07	14•34	$Na_5P_3O_{10},6H_2O$

TABLE XXIV. - CONDUCTIVITY DATA FOR SODIUM TRIPHOSPHATE

Concentration	Conductivities		
	Molecular	Equivalent	Equivalent (corrected)
N/32	89•5	68•42[205]	-
N/64	96•1	79•08[205]	-
N/128	103•0	89•35[205]	-
N/256	-	99•19[205]	-
N/512	-	109•93[205]	-
N/1024	-	117•41[205]	-
0•0027496N	-	120•6	120•1[248]
0•0017765N	-	127•4	126•4[248]
0•0011377N	-	133•9	132•6[248]
0•0009102N	-	137•9	136•5[248]
0•0007098N	-	140•3	138•6[248]
0•0005562N	-	143•5	140•4[248]
0•0003051N	-	149•7	-
0•0001940N	-	153•1	-
0	-	-	159•0[248]

the triphosphoric acid the first three hydrogen ions to be strong, the fourth to be comparable with the third of pyrophosphoric acid and the fifth to be slightly stronger than the fourth of pyrophosphoric acid.[163] Paper chromatographic data are also presented in Table VII.[22]

The effects of the salt on the sinking time of oil-soaked cotton in aqueous solutions,[257] on the micellar molecular weights of dodecyl benzenesulphonate (which are increased on addition of the salt),[285] on the peptization of Prussian Blue,[286] on the infra-red absorption of skeletal muscle[287] and on the dispersion of soil particles[150] have also been described.

Chemical Properties.

The effect of heat on sodium triphosphate hexahydrate is of some interest: it had been supposed that the product obtained on heating the salt at 120° for some days was a sodium dimetaphosphate, isolated as its tetrahydrate after extraction with water and precipitation with alcohol.[205] This, however, has been shown to be incorrect, and an intergrown mixture of sodium ortho- and pyro-phosphates is produced. An approximate overall reaction has already been given (see page 1297).[163] It is believed that at 100°C. five molecules of water are lost as follows:-

$$Na_5P_3O_{10},6H_2O \rightarrow Na_3HP_2O_7 + Na_2HPO_4 + 5H_2O$$

accompanied by hydrolysis of the triphosphate by the sixth molecule of water.[20,21] Owing to the favorable juxtaposition of the anionic products, interchange between sodium and hydrogen can occur on further heating to 120°C.:-

$$Na_3HP_2O_7 + Na_2HPO_4 \rightarrow Na_4P_2O_7 + NaH_2PO_4$$

This has been confirmed by density and cryoscopic measurements.[20] The products are still intergrown and on further heating they recombine, rapidly at 170°C.,[19] with elimination of water[18] to give the sodium triphosphate-II accompanied by minor quantities of disodium dihydrogen diphosphate which are due to molecular dehydration of the acid orthophosphate:-

$$\begin{gathered} Na_4P_2O_7 + NaH_2PO_4 \rightarrow Na_5P_3O_{10} + H_2O \text{ and} \\ 2NaH_2PO_4 \rightarrow Na_2H_2P_2O_7 + H_2O \end{gathered}$$

On further heating to above 450°C. the triphosphate is converted into type-I and at the same time the product becomes almost exclusively triphosphate owing to one of the following reactions:-

$$\begin{gathered} Na_2H_2P_2O_7 + 2Na_4P_2O_7 \rightarrow 2Na_5P_3O_{10} + H_2O \text{ or} \\ 2xNa_2H_2P_2O_7 \rightarrow 2(NaPO_3)_x + xH_2O, \text{ followed by} \\ (NaPO_3)_x + xNa_4P_2O_7 \rightarrow xNa_5P_3O_{10} \end{gathered}$$

The first step in this sequence can be observed in sodium triphosphate hexahydrate that has been stored in a stoppered bottle over a long period, when a further reaction without formation of orthophosphates may occur:-[21]

$$2Na_5P_3O_{10} + H_2O \rightarrow Na_4P_2O_7 + 2Na_3HP_2O_7$$

Attempts to effect ring-closure converting the triphosphate to sodium trimetaphosphate, i.e., the reversal of one method of preparation, have not been successful.[251]

Hydrolysis in aqueous solution leads to a mixture of sodium acid orthophosphate and acid pyrophosphate:-[163]

$$Na_5P_3O_{10} + H_2O \rightarrow Na_3HP_2O_7 + Na_2HPO_4,$$

and ultimately to acid orthophosphates alone. The hydrolysis is of zero order and slow at room temperature[21] or of first order at constant hydrogen ion concentration at 65°C.[170] The reaction is acid-base catalyzed.[164] A decrease in pH and a rise in temperature increase the rate of hydrolysis,[172,175,288] but the salt is fairly stable in alkaline solutions,[8] with a maximum stability at pH 10.[172] The stability is less than that of pyrophosphate, but greater than that of tri-, tetra- and poly-metaphosphates under similar conditions.[8,254] Typical hydrolysis data for the commercial product (92%, 2% and 6% respectively of the triphosphate, orthophosphate and pyrophosphate) have been published.[8,171] Fig. 10 shows the relative rates of hydrolysis of sodium triphosphate and sodium polymetaphosphate glass in aqueous solution:[8] the salt is approximately 50% hydrolyzed ('reverted') after 6 hours at 100°C. in water, and 15% after 60 hours at 70°C.[10] The relatively rapid hydrolysis in dilute nitric acid solutions is employed in the determination of triphosphate; the resulting orthophosphate is determined by standard methods.[182] Presence of calcium ions increases the rate of hydrolysis, the effect varying with pH, but magnesium ions appear to have no effect.[175]

In fairly concentrated solution, di- and tri-valent cations are normally precipitated by addition of sodium triphosphate in aqueous solution, but the precipitated triphosphate of the cation usually dissolves in a slight excess of the sodium triphosphate.[8] The solutions contain a complex salt in which the metal appears in the anion. This has some practical application in removing

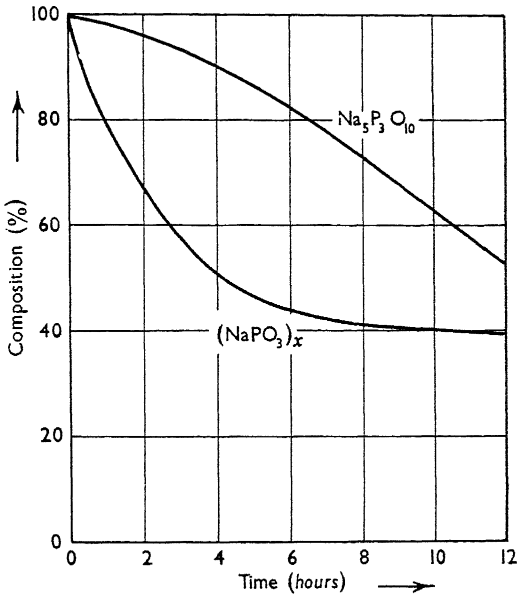


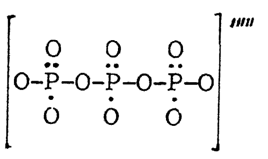
FIG. 10. HYDROLYSIS OF SODIUM TRIPHOSPHATE AND GLASSY POLYMETAPHOSPHATE IN 1% AQUEOUS SOLUTION AT 100°C.

the hardness of water, presumably by formation of complexes such as $[\mathrm{CaP_3O_{10}}]'''$,[21,270,288] and in the removal of iron impurities as $[\mathrm{FeP_3O_{10}}]''$[66,71,273] with an efficiency greater than that of tetrasodium pyrophosphate and some metaphosphates:[246] 1·2 pounds of the salt will soften a quantity of water containing 1000 grains of hardness,[247] and to prevent precipitation from a solution containing 100 p.p.m., 417 p.p.m. of sodium triphosphate are required (cf. 306 for polymetaphosphate glass and 800 for pyrophosphate).[123] The dissociation constant of the complex ion $[\mathrm{CaP_3O_{10}}]'''$ is given as $2{\cdot}1 \times 10^{-7}$ at 60°C. and $3{\cdot}1 \times 10^{-7}$ at 30°C.,[21] and this is sufficiently low to prevent the solubility product of calcium oxalate being exceeded,[8,164] as is true also for certain calcium fatty acid soaps[254,289,290] and for gypsum,[31,271] although the presence of precipitating ions in detergent compositions, e.g. orthophosphate, tends to reduce the sequestering power of the triphosphate[32] and the efficiency decreases with increasing concentration of triphosphate,[21,32] possibly owing to the formation of complexes such as $\mathrm{Ca[Na_4P_3O_{10}]_2}$ at pH 8 to 9[290] or $\mathrm{NaCa_2P_3O_{10}}$ and $\mathrm{Ca_3(P_3O_{10})OH,5H_2O}$.[21] In suppressing calcium carbonate deposition or calcite scale dissolution and in detergency, presumably the same mechanism of ion association of the cation upon the flexible polyphosphate chain still operates, but the mode of action is complicated by the simultaneous operation of a surface effect. The triphosphate anion, because of its multiple negative charges, is strongly adsorbed on many surfaces and it has been pointed out that the repeating O–P–O–P–O–P–O unit of the ionic chain has the proper spacing for ready adsorption on the calcite lattice: this prevents further growth of nuclei at an early stage of crystallization.[30] In some processes calcium is deliberately introduced into the reaction mixture for preparing sodium triphosphate for various detergent and kindred purposes.[235,237]

Removal of barium ions by sodium triphosphate has been investigated polarographically and evidence has been produced for the formation of the insoluble salt $Ba_5(P_3O_{10})_2$[28,205,291] and the soluble compound $Na_3BaP_3O_{10}$;[28,291] under normal conditions, no precipitate is obtained and this is the basis of the analytical separation of triphosphate from other sodium phosphates.[182] When magnesium ions are added to a solution of the salt, there is a marked drop in the pH of the solution to approximately 6·5 where the drop is arrested; the solutions give precipitates on boiling but these redissolve on cooling.[292] The sparingly soluble salt $NaZn_2P_3O_{10}$ readily forms supersaturated solutions and can be precipitated only after seeding and prolonged digestion, thus permitting the analytical separation of pyrophosphate (as insoluble normal zinc pyrophosphate) from triphosphate.[191] Conductimetric measurements during addition of cobalt and nickel ions to a solution of sodium triphosphate show a distinct break corresponding to the formation of the ions $NiP_3O_{10}{}'''$ and $CoP_3O_{10}{}'''$[205] and the dissolution of manganous carbonate, especially in hot solutions of the triphosphate, has been ascribed to the formation of the complex $MnNa_3P_2O_{10}$.[8] Other double salts that have been isolated are: $CdNa_3P_3O_{10},12H_2O$,[205,245] $CrNa_2P_3O_{10},6H_2O$,[205,245] $Mn_5(P_3O_{10})_2$, $Na_3ZnP_3O_{10},11{\cdot}5H_2O$, $NaZn_2P_3O_{10},9{\cdot}5H_2O$, $NaCd_2P_3O_{10},7H_2O$, $NaCa_2P_3O_{10},4H_2O$, $Pb_5(P_3O_{10})_2$, $Na_8Pb(P_3O_{10})_2,14H_2O$, $NaSr_2(P_3O_{10}),7H_2O$, $Sr_5(P_3O_{10})_2$, $NaBe_2P_3O_{10},5H_2O$, $Be_5(P_3O_{10})_2$, $Na_3CuP_3O_{10},12H_2O$, $Cu_5(P_3O_{10})_2$. Aluminium salts give no precipitate.[205] *X*-Ray measurements have been made on the double salts $NiNa_3P_3O_{10}$, $Ni_2NaP_3O_{10}$ and $(NH_4)NaP_3O_{10}$. The tetra-ammonium sodium triphosphate is converted into the diammonium trisodium salt with sodium hydroxide; on heating this salt yields mainly the insoluble sodium metaphosphates $NaPO_3$-III and II.[251] The formation of salts with divalent ions of the type $Na_3MP_3O_{10}$ is in agreement with the observation that in triphosphoric acid there are three strongly acidic and two weakly acidic protons, as shown by electrometric titration.[128]

Sodium triphosphate forms an addition compound with hydrogen peroxide, $Na_5P_3O_{10},H_2O,2H_2O_2$, on evaporating a solution of the constituents.[205] With tris(ethylenediamine)cobalt(III) ion, the triphosphate, but not the pyrophosphate, gives a precipitate which can be used in the gravimetric and colorimetric determination of triphosphate.[21] Actomyocin gives triphosphate complexes having a dissociation constant of $23{\cdot}7 \times 10^{-6}$ and, in the presence of magnesium sulphate (0·001M), $3{\cdot}7 \times 10^{-6}$.[293] The precipitation of salts of sodium triphosphate with simple organic and inorganic bases at pH 2 to 4 has been investigated.[294] The corrosive action of sodium hydroxide on glass in the presence of the salt has been examined.[86]

A survey of these chemical and physical properties, especially the hydrolysis products, the individuality of the triphosphate anion, and molecular weight and electrometric titration data, leads to the following most probable structure:-[128,163,164]



$$\left[\mathrm{O{-}\underset{\dot{O}}{\overset{O}{\ddot{P}}}{-}O{-}\underset{\dot{O}}{\overset{O}{\ddot{P}}}{-}O{-}\underset{\dot{O}}{\overset{O}{\ddot{P}}}{-}O}\right]^{''''}$$

in its classical form. The terminal groups provide the source of the two weakly acidic protons.

The salt has been examined microscopically and described for analytical purposes,[181] but microscopic identification in the presence of other compounds is not reliable.[163] Methods have been described for **assaying** the salt for its solubilizing effect on calcium oleate[295] or by precipitating with calcium chloride.[123] In solution a pH titration method based on the reaction:-

$$Na_5P_3O_{10} + 2H^{\bullet} \xrightarrow{pH 3{\cdot}8} Na_3H_2P_3O_{10} + 2Na^{\bullet} \text{ followed by}$$
$$Na_3H_2P_3O_{10} + Zn^{\bullet\bullet} \rightarrow Na_3ZnP_3O_{10} + 2H^{\bullet}$$

has been described,[10,191,296] as has a radiophosphorus radioisotope dilution method.[200] In complex solutions, other phosphates are determined by standard methods and the total phosphorus is determined by hydrolytic conversion of all phosphates to orthophosphate which is assayed by the ammonium phosphomolybdate method: triphosphate is obtained by difference.[182] Not only have *X*-ray techniques been of diagnostic value, but they also have analytical applications.[19,21,118,246,280,281] Critical reviews of available methods have been published.[21,198]

Sodium Hydrogen Triphosphates, Acid Sodium Tripolyphosphates

Hydration of sodium trimetaphosphate is said to yield trisodium dihydrogen triphosphate in aqueous solution[171] or by heating the monohydrate at 120°,[251] as does the action of dilute acid (at pH 3·8) on the normal triphosphate.[128,191] Treatment of the normal salt with acetic acid in aqueous ethanol causes the separation of an oil which ultimately crystallizes to give a product corresponding to the acid salt $Na_5P_3O_{10},Na_3H_2P_3O_{10},3H_2O$, from which the normal salt can be separated: it has been suggested that the acid salt may be an intermediate in the molecular dehydration of sodium dihydrogen orthophosphate or disodium dihydrogen diphosphate.[297] Traces of acid sodium triphosphates may well be present in sodium polymetaphosphate glass which has been prepared in moist air, thus accounting for approximately 1% of water which is only expelled during the thermal conversion to trimetaphosphate.[164] An attempt to prepare the acid salt by treating trisodium cobalt triphosphate with hydrogen sulphide was not successful.[205] Heating sodium dihydrogen orthoarsenatophosphates, $NaH_2(As,P)O_4$, is said to give acid triarsenatophosphates such as $Na_3H_2(As,P)_3O_{10}$ as intermediates, provided that the arsenic to phosphorus ratio is $\gg 2:1$.[223]

The effect of heat on the hydrates, $2Na_3H_2P_3O_{10},3H_2O$ and $2Na_4HP_3O_{10},3H_2O$, is analogous to that on the hexahydrate of the normal salt: hydrolysis to ortho- and pyro-phosphate mixtures occurs, but the products readily undergo molecular dehydration, e.g.:-

$$2Na_3H_2P_3O_{10},3H_2O \rightarrow 2(NaPO_3)_3 + 8H_2O$$[19]

In solution the salt is readily converted by acid hydrolysis into sodium orthophosphates, and into sodium dihydrogen orthophosphate in water[171] and is converted into the normal salt by addition of sodium hydroxide.[171]

No other acid salts of sodium triphosphate have been reported.

SODIUM TETRAPHOSPHATE, SODIUM TETRAPOLYPHOSPHATE (AND HIGHER POLYPHOSPHATES)

Several claims have been made for the preparation of hexasodium tetraphosphate (and higher polyphosphates) by heating mixtures containing sodium oxide and phosphorus pentoxide in the ratio of 3:2 (or suitable variations for other polyphosphates in the series $Na_{n+2}P_nO_{3n+1}$) in a manner analogous to the preparation of the normal sodium triphosphate, e.g., [298,299]. This might be achieved by heating trisodium hydrogen pyrophosphate to 300°[202] or by heating suitable mixtures of tetrasodium pyrophosphate and sodium metaphosphates: later work has shown that the products on cooling are mixtures of sodium triphosphate with sodium pyro- or meta-phosphates under almost any conditions of preparation.[28,115,120,163,164,171,205,246,283,291] This does not exclude the possibility that in these mixtures the tetraphosphate has only a limited range of thermal **stability.**[163] Typical analytical data for sodium tetra- and septa-phosphates of commercial manufacture are given in Table XXV.

TABLE XXV. - ANALYSES OF SODIUM POLYPHOSPHATE GLASSES

Salt	Percentage Composition of Sodium Polyphosphate			
	Tetra-[8]	Tetra-[191]	•Septa-[191]	Septa-[8]
Trisodium orthophosphate	}5	5•0	2•0	–
Tetrasodium pyrophosphate		3•0	–	–
Pentasodium triphosphate	61	58•0	45•0	50
Sodium polymetaphosphate	22	16•0	54•0	50
Sodium trimetaphosphate	12	–	–	–
Total phosphorus	–	27•3	27•8	–
Undetermined	–	18•0	–	–

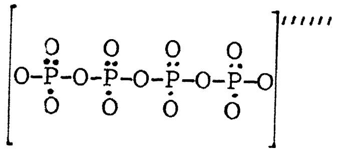
An alternative suggestion, fusion hydrolysis of sodium 'hexametaphosphate' (true polymeric state not known) with sodium hydroxide,[300] has not been substantiated, but alkaline hydrolysis of sodium tetrametaphosphate could **lead** to the desired product in a reaction analogous to the alkaline hydrolysis of sodium trimetaphosphate to sodium triphosphate:-[21,248,301]

$$Na_4P_4O_{12} + 2NaOH \rightarrow Na_6P_4O_{13} + H_2O$$

The reaction must be carried out in sodium hydroxide solution at 25° to 28°C., with a 100% excess of the alkali:[21] paper chromatography affords evidence that up to 60% of the hydrolysate is the tetraphosphate.[25,302] The product is very soluble in water (at least to an extent of 44%); the commercial material called tetraphosphate has a solubility exceeding 150g. per 100g. of water at room temperature.[123] The salt forms no crystals convenient for its purification.[21] Excess caustic soda and high temperatures probably increase the rate of hydrolysis of the tetrametaphosphate but the competitive hydrolytic breakdown to two molecules of tetrasodium pyrophosphate and, ultimately, to orthophosphate becomes predominant.[21] Reference has been made to a separation of 'crude' sodium tetraphosphate from other sodium phosphates by paper electrophoresis.[26]

Despite the non-existence of true sodium tetraphosphate in the commercial polyphosphate glass produced by thermal means, preparations known as tetraphosphate together with other unsubstantiated higher polyphosphates find numerous applications in detergent compositions,[33,53,259,299,303-305] in sequestration of ions such as calcium[32,123] and other[306] ions, as a dispersing[8,150,300,307] or deflocculating[307-309] agent and in pH control.[310] Its effect is due to the properties of the constituent polymetaphosphates or sodium triphosphate.

The pH of a 1% solution of the commercial material is 7•4, and data for hydrolysis and sequestering power have been given.[123] The commercial salt, in aqueous solution, gives a cloudiness with barium chloride after 15 minutes, in contrast to the lack of any precipitate with sodium triphosphate.[182] A thio derivative, $Na_6P_4O_{10}S_3$, has been mentioned.[303,308] By analogy with the di- and tri-phosphates, the tetraphosphate would be expected to have, in its classical form, the structure:-



$$\left[\mathrm{O{-}\overset{O}{\underset{O}{P}}{-}O{-}\overset{O}{\underset{O}{P}}{-}O{-}\overset{O}{\underset{O}{P}}{-}O{-}\overset{O}{\underset{O}{P}}{-}O}\right]^{\prime\prime\prime\prime\prime\prime}$$

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SODIUM METAPHOSPHATES

Over the past thirty years the chemistry of sodium metaphosphate, $(NaPO_3)_n$, has caused a great deal of controversy, largely owing to uncertainties as to the value of n and the structure of the anion and, to a lesser extent, to confusion with the true polyphosphates. At least nine distinct chemical or physical entities (ignoring hydrates) known as 'sodium metaphosphate' have been described, and uncorroborated evidence has been published for some others. In this account the nomenclature proposed by Partridge[1] is employed, not so much because of its less arbitrary nature as compared with other systems, but chiefly because of its more common usage.

Many of the sodium metaphosphates are prepared by the action of heat on disodium dihydrogen diphosphate, the reaction being, in its simplest form:-

$$Na_2H_2P_2O_7 \rightarrow 2NaPO_3 + H_2O.$$

This simple reaction must, however, be elaborated as follows:-

$$\begin{tikzcd}
 & Na_2H_2P_2O_7 \arrow[d, "<260^\circ"', "-H_2O"] & \\
 & (NaPO_3)_2(?) \arrow[d, "260^\circ"'] & \\
 & NaPO_3\text{-III (insoluble)} \arrow[d, "300\text{–}400^\circ"'] & \\
 & NaPO_3\text{-II (insoluble, 'Maddrell salt')} \arrow[d, "400\text{–}628^\circ"'] & \\
 & NaPO_3\text{-I (soluble, } Na_2P_3O_9\text{)} \arrow[d, ">628^\circ"'] & \\
\text{Fibrous } NaPO_3 \text{ ('Kurrol salt')} & NaPO_3 \text{ melt} \arrow[l, "\text{cool}" above, "\text{seed}" below] \arrow[r, "\text{chill}"] & NaPO_3 \text{ glass ('Graham salt')}
\end{tikzcd}$$

There is no clear-cut temperature, except the melting point, at which interconversion occurs; some of the changes are reversed on cooling over a prolonged period, and minor variations are also possible by choice of cooling conditions.

Sodium Monometaphosphate

Several procedures for the preparation of the monomer have been described, but the products have been demonstrated at a later date to be other forms of the metaphosphate. Thus, addition of phosphorus pentoxide to ether gives hexameric ethyl metaphosphate, $(C_2H_5PO_3)_6$, which with sodium ethoxide is said to yield monomeric sodium metaphosphate:[2,3] the formula was supported by cryoscopic evidence, but later work casts great doubt on this evidence.[4] The conclusions have been refuted[5] and the product has been shown to be sodium trimetaphosphate by conductivity measurements.[6] Analogous decomposition of 'true' sodium hexametaphosphate (of extremely dubious existence) to the monomer has also been claimed.[7] A thermal method,[8,9] backed by scanty physical evidence, is also said to yield the monomer, but the product is almost certainly the trimer.[6] The need of 'special' methods of preparing[10] and separating[11] the monomer has been recognized. Hydrolysis of the supposed monomer *via* the pyrophosphate[12] to the orthophosphate is said to be a first order reaction:[13] this property is to be expected of the trimer.

The presence of the monomeric anion PO_3 has been claimed in the dissociation of tetrasodium pyrophosphate in lithium metaborate melts.[14]

Sodium Dimetaphosphate

Several references have been made to the dimetaphosphates but these are largely uncorroborated and the existence of these salts is not certain.[5] The dimetaphosphate described by Fleitmann (Mellor,II,868) has been shown to be sodium tetrametaphosphate.[3,15] A dimetaphosphate, $(NaPO_3)_2,3H_2O$, is said to be obtained by heating phosphoric acid to 320°C. for a short time, then treating this with sodium hydroxide and precipitating with ethanol. Evidence for the formation of this salt rests on its high solubility and on conductivity measurements.[16] It has been suggested that the insoluble sodium metaphosphates ($NaPO_3$-III and -II) when heated to 270° to 450°C. for some time tend to give a soluble form that might be a dimetaphosphate.[17] Thermal decomposition of sodium triphosphate hexahydrate at 120° to 300°C. is said, on cryoscopic evidence, to give the dimer:-[15,18]

$$2Na_5P_3O_{10} \rightarrow 2Na_4P_2O_7 + (NaPO_3)_2;$$

but this is not agreed by other authors.[19-22] Similarly, on heating 1:1 mixtures of ammonium nitrate and disodium hydrogen orthophosphate to 236° a product is obtained which is soluble in water from which it can be precipitated with ethanol as an oil which finally crystallizes as the hydrate $Na_2(PO_3)_2,3H_2O$;[16,23-25] the salt $Na_4P_2O_6$ may be an intermediate in this reaction, since at 236° this is converted to the supposed dimer in the presence of sodium nitrate. It was concluded from this work that sodium dimetaphosphate should be present in the low-temperature decomposition products of monosodium dihydrogen orthophosphate[18,23,26] and this has been confirmed at temperatures below 260°[27] by several physical methods. It has been pointed out, however, that the dimeric form is not likely to be formed by thermal means owing to the strain in a dimetaphosphate ring structure; larger rings with less strain are more likely to be formed.[28] An unstable dimer readily hydrated to disodium dihydrogen diphosphate[15,29] is said to be the first product obtained on heating tetrasodium diphosphate with phosphorus pentoxide. Similarly, a dimetaphosphoric acid may be formed on dissolving phosphorus pentoxide in moist ether and the resulting acid can be converted into its sodium salt *via* its lead salt,[30] but conductivity measurements indicate the sodium salt to be an impure trimer.[6] A claim[30] that the dimetaphosphate can be prepared by melting disodium hydrogen orthophosphate dodecahydrate with ammonium chloride and ammonium nitrate must be regarded as unsubstantiated,[15] especially in view of conductivity measurements that indicate the product to be the trimetaphosphate in an impure form (Λ_0 133·5).[6] The action of heat on sodium hydrogen methyl (or ethyl) orthophosphates is also said to yield the dimer.[15] The dimer may be an intermediate in the hydrolysis of sodium polymetaphosphate in aqueous solution, the final product being orthophosphate.[31]

Heating the hydrates of the dimer causes either dehydration at 200° C.[15] or hydrolysis to acid pyrophosphate with subsequent successive conversion to insoluble tri- and poly-metaphosphates with increasing temperature.[15,16,23] The instability of sodium dimetaphosphate in aqueous solution has been recognized,[11] and its hydrolysis can be used in the preparation of disodium dihydrogen diphosphate.[32] At 20·5° C. equivalent conductivities have been given as 75 and 55 at concentrations of N/1024 and N/32, respectively, thus apparently confirming its basicity according to Ostwald's rule.[16,31] Luteocobaltic salts in neutral solution do not give a precipitate with the salt; the zinc salt is soluble in excess of the sodium dimetaphosphate in aqueous solution and, in the presence of acetic acid, the dimer does not coagulate albumen.[16] Action of sodium hydroxide or of trisodium orthophosphate on the salt causes hydrolysis to the normal pyrophosphate, for example:-[33,34]

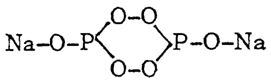
$$Na_2P_2O_6 + 2Na_3PO_4 \rightarrow 2Na_4P_2O_7.$$

With sodium nitrate the trimeric sodium metaphosphate is ultimately formed:-[23,24]

$$6NaNO_3 + 3(NaPO_3)_2 \xrightarrow{\geq 320^\circ} 3Na_4P_2O_7 + 3N_2O_5 \text{ followed by}$$
$$3Na_4P_2O_7 + 3N_2O_5 \rightarrow 2(NaPO_3)_3 + 6NaNO_3;$$

although, at 260° to 300° C., a 'true' crystalline hexametaphosphate may also be an intermediate. With sodium halides in the presence of air at 650° to 750° C., the halogen and tetrasodium diphosphate result; again, at lower temperatures, polymerization may occur. The reaction is catalyzed by silica, and analogous reactions with calcium and potassium iodides have been described.[24,25,34,35]

A structural formula:-



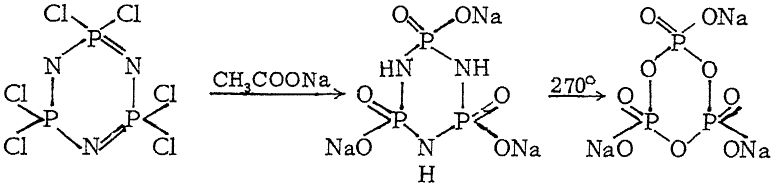
has been suggested,[29] and some literature references to the trimetaphosphate have been claimed as being truly concerned with the dimer,[17,29,33] although the weight of present evidence would suggest the opposite view.

Sodium Trimetaphosphate

Preparation.

Heating sodium dihydrogen orthophosphate leads to the formation of disodium dihydrogen pyrophosphate, which between 530° and 628° C. loses the elements of water to yield sodium trimetaphosphate $(NaPO_3)_3$, $NaPO_3$-I, almost exclusively. At lower temperatures the trimer is a constituent, in variable proportions, of mixtures containing the insoluble sodium metaphosphates III and II,[6,18,22,26,27,36-44] or, possibly, some acid polyphosphates.[45] Lower temperatures but prolonged heating times have also been recommended,[38,41] but it has been pointed out that reversion to the insoluble forms can occur at 400° C.[42] Similar results are achieved on heating a mixture of disodium hydrogen orthophosphate (60g.) and ammonium nitrate (17g.) to 300° C. or, better, to temperatures just below the fusion point of sodium metaphosphate.[10,15,18,36,37,46] Most other forms of the sodium metaphosphates revert rapidly to the trimer on 'tempering' at 300° to 625° C. (most efficiently at 575° to 625° C.); this is true, for example, for the insoluble polymetaphosphates II and III,[16,36,38,47-50] the soluble polymetaphosphate, Graham's salt,[18,36,44,51-54] the fibrous polymetaphosphates, Kurrol salt,[21,37,55] or the sodium tetrametaphosphate (at 400°C.).[56] Some trimer invariably accompanies fibrous and glassy metaphosphates when these are prepared by cooling the molten metaphosphate.[22,55] An insoluble form of the trimer is said to be formed on heating disodium dihydrogen diphosphate below 250°,[36] but this may have been confused with insoluble polymeric forms that would almost certainly have been present at the same time.

Heating trisodium dihydrogen triphosphate hydrates gives sodium trimetaphosphate in good yield at temperatures above 250°C., but similar reactions are not observed with the normal salt.[21,57] The trimer may also be prepared by the action of sodium chloride on silver trimetaphosphate followed, after filtration, by precipitation of the salt with ethanol[58] or, possibly, by heating monosodium dialkyl orthophosphates at 400°C.[15,59] At least two methods[2,3,8] which are claimed to give the monomeric metaphosphate actually yield the trimer in an impure form. Of considerable interest in the elucidation of the structure of the trimetaphosphate anion is the following sequence in which phosphorus nitrogen dichloride is treated with sodium acetate for 10 days and the resulting phosphimate is hydrolyzed at 270°C. for 100 hours to the trimetaphosphate *via* the intermediate $Na_3[P_3(NH)_2O_7]$:-[60]



The trimer has not been found in acid or strongly alkaline hydrolysates of the long-chain polymetaphosphates, but it is present in such mixtures from neutral or slightly alkaline solution,[55] the trimetaphosphate accounting for one sixth of the products.[61]

Two unstable polymorphic forms, I′ and I″, of the salt, recognized by *X*-ray and refractive index characteristics, are formed on controlled cooling of the metaphosphate melt: I′ is formed between 500° and 525°C. and I″ between 375° and 525°C. They differ only in crystal form and in solution exhibit identical properties.[54]

The hexahydrate is readily prepared by direct hydration of the anhydrous salt at room temperature or, better, below 10°C. in the presence of sodium chloride.[18,39,44,57,62] A monohydrate is obtained on crystallization of the anhydrous salt from water above 30°C.[57] and a sesquihydrate, a hemihydrate and an unstable monohydrate have also been described.[62]

Separation of sodium trimetaphosphate from other metaphosphates is normally achieved by dissolution in and crystallization from water, since most of the other metaphosphates likely to be present are almost insoluble. Small scale separations by paper chromatography have also been described.[11,63-66]

Uses.

Sodium trimetaphosphate displays none of the desirable cation-sequestering properties possessed by other chain-type polymeta- and poly-phosphates of sodium. Its use is limited to its intermediary role in the preparation of the useful sodium triphosphate.

Physical Properties.

Debye diagrams for the three forms of the anhydrous salt and for the hydrates have been published.[1,54,62] The hexahydrate has a lattice constant of 10·84A. parallel to the longest rhombohedral edge; the monohydrate, which is tetragonal bipyramidal, has: a = 7·99 and b = 13·14A. with a unit lattice volume of 839cu.A. and $z = 3{\cdot}98$ formula units of salt.[62] The hexahydrate crystallizes in the triclinic system with two formula units per unit cell and $a = 8{\cdot}41$, $b = 10{\cdot}92$ and $c = 9{\cdot}86$A., with angles $\alpha = 67^\circ\ 51'$, $\beta = 92^\circ\ 6'$ and $\gamma = 106^\circ\ 10'$.[67] In the crystal, the distance O″ to Na˙ is nearly equal intra- and inter-molecularly, so that the bonds may be represented as $-\mathrm{Na{-}O{-}\overset{|}{\underset{|}{P}}{=}O\cdots\cdot Na{-}O{-}\overset{|}{\underset{|}{P}}{=}O\cdots}$. *X*-Ray studies show that the constitution is unchanged on passing into solution and that the cyclic structure of the trimetaphosphate system is recognizable in higher polymers.[66]

Optical data for sodium trimetaphosphates are given in Table XXVI. It is of interest to note that a substance once claimed to be the monomer and now shown to be an impure trimer has N_g 1·486 and N_p 1·473.[9]

TABLE XXVI. - OPTICAL DATA FOR SODIUM TRIMETAPHOSPHATE

Salt	Optic sign[68,69]	Optical angle[68,69]	α
Anhydrous salt	–	80°	1·474,[68,69] 1·471[44]
Monohydrate	–	–	1·499[56]
Hexahydrate	–	77°	1·432,[68] 1·433[44,56]

Salt	β	γ	N_g	N_p
Anhydrous salt	1·478,[68,69] 1·476[44]	1·480[44,68,69]	1·480	1·474
Monohydrate	1·500[56]	1·504[56]	–	–
Hexahydrate	1·442[44,56]	1·441,[68] 1·446[44,56]	–	–

Characteristics of the infra-red absorption spectrum are presented in Table XXVII.[70]

TABLE XXVII. - INFRA-RED ABSORPTION BANDS OF SODIUM TRIMETAPHOSPHATE

$Na_3P_3O_9$		$Na_3P_3O_9,H_2O$	
Wave number (cm.$^{-1}$)	Intensity	Wave number (cm.$^{-1}$)	Intensity
1314	strong, sharp	3465	medium
1298	very strong	1680	weak, broad
1262	strong	1610	weak, broad
1169	strong	∼1315	medium
1162	strong	1292	very strong
1120	strong, sharp	1260	very strong
1101	–	1158	medium
987	very strong, broad	1112	strong
773	very strong	1100	strong
757	very strong	970	very strong, broad
686	strong	774	strong
		755	strong
		695	medium

$Na_3P_3O_9,6H_2O$		$CaNaP_3O_9,3H_2O$	
Wave number (cm.$^{-1}$)	Intensity	Wave number (cm.$^{-1}$)	Intensity
3485	strong	3580	weak
∼1640	weak, broad	1655	medium

continued on following page

TABLE XXVII (continued)

$Na_3P_3O_9, 6H_2O$		$CaNaP_3O_9, 3H_2O$	
Wave number (cm.$^{-1}$)	Intensity	Wave number (cm.$^{-1}$)	Intensity
1312	medium	1625	strong
1294	very strong	1320	medium
1270	strong	1303	very strong
1159	medium	1275	very strong
1100	strong	1168	medium
975	very strong, broad	1116	strong
776	strong	1012	strong, broad
756	strong	900	very weak
698	medium	772	very strong
		767	strong
		~700	weak

Raman spectra show a main frequency of 1154 and other frequencies of 1244 and 660 cm.$^{-1}$, these being attributed to the asymmetric PO_2 vibration and the symmetric vibration of the ring oxygen atoms.[71] These spectra are in accord with a planar, but not with a boat or chair, ring structure for the trimetaphosphate anion.[72]

The density of the hexahydrate is given as 1·786.[67] The microcrystalline form of sodium trimetaphosphate has been described for analytical purposes:[73] the hexahydrate consists of rhombohedra with an oblique extinction and a silhouette angle of 70°–75°.[68] No exchange of phosphorus was observed between the trimer and other polymetaphosphates at 0° and 25°C. by radiotracer techniques.[74]

Solubility at 517°C. is given as 0·96 weight fraction of sodium trimetaphosphate in water by the closed tube method.[75] Densities of solutions in water up to 0·01N. are given by the expression $d_4^{25} = 0{\cdot}99707 + 0{\cdot}0695c$, where c is equivalent concentration.[6] Cryoscopy in water[4,18] and at the sodium sulphate decahydrate eutectic[15] shows the molecular weight to be approximately 310, in accord with the trimeric formula ($Na_3P_3O_9 = 306$). At pH 6·35 the product of diffusion coefficient reduced to 10°C. and the viscosity is given as 0·638, and at pH 4·7 the dialysis coefficient is 0·539.[5] Conductivity data are given in Table XXVIII. These lead to the conclusion that the salt is uni-tervalent, and Λ_0 is 133·70 of which 83·59 is contributed by the trimetaphosphate anion. The dissociation constant of the parent acid (k_3) is 0·068.[6]

TABLE XXVIII.- CONDUCTIVITY DATA FOR SODIUM TRIMETAPHOSPHATE

Concentration (molality)	Conductivity (χ) (0° C.)[18]	Equivalent concentration	Equivalent conductivity (25° C.)[6]
0·0010048	0·00018085	0·00011767	130·52
0·0039883	0·00064756	0·00024321	129·08
0·010383	0·0015205	0·00034824	128·13
0·021752	0·0029081	0·00047290	127·15
0·042593	0·0051955	0·00087976	124·74
0·060286	0·0069755	0·0014061	122·46
0·083238	0·0091369	0·0024782	119·25
0·10149	0·010758	0·0039445	115·94
0·15410	0·015031	0·0065290	111·83
0·20147	0·018440	0·0081721	109·76
0·30773	0·025020	0·014255	104·19

It has been pointed out that the unsuitable geometry of the anionic structure prevents adsorption on calcite so that the trimer is ineffective in preventing calcite deposition.[76,77] Paper chromatographic data are summarized in Table VII.[65] (see page 1272).

Chemical Properties.

The effect of heating on sodium trimetaphosphate is of considerable interest: up to 628°, the m.p., no apparent change takes place, unless the temperature is maintained at 400°C. for a long time,[42] but immediately fusion takes place sodium polymetaphosphate of high molecular weight is produced.[26,42] It has been claimed that a tetrametaphosphate is an intermediate in this change and that fibrous Kurrol salts can be formed directly from the trimer[78,79] but this has not been substantiated.[5,42,49,53] The effect of heat on the hydrates is more complex and is not fully established: the hexa- and sesqui-hydrates are readily dehydrated to the anhydrous salt on gently heating (the hexahydrate dissolves in its water of crystallization at 53°C., but dehydration is complete after some time at 50°C.[44]) without obvious structural change,[61,62] as are the mono-hydrates, the metastable form decomposing at 80° to 110°C. and the stable form at 50° to 100°C. At approximately 120° after rapid heating, however, the monohydrates lose 0·3 molecules of water and hydrolyze to a mixture of ortho- and tri-phosphate; at 140° to 150° some diphosphate may also be formed. Above 150°C. all the water is driven off and between 200° and 300°C. trimetaphosphate, in its anhydrous form, is re-formed,[62] by a reaction analogous to the thermal dehydration of acid sodium triphosphate.[21]

The binary system $NaPO_3$-KPO_3, in which the sodium metaphosphate starting material is probably the trimer, has been investigated. A double compound, $3NaPO_3,KPO_3$, m.p. 552°C., was recognized. Optical properties are given in Table XXIX.[52]

TABLE XXIX. - OPTICAL PROPERTIES IN THE $NaPO_3$-KPO_3 SYSTEM

Salt	Optic sign	2V	α	ω	β	ε	γ
Sodium tri(?)metaphosphate	-	80°	1·474	-	1·478	-	1·480
Double compound $3NaPO_3,KPO_3$	-	40°	1·493	-	1·500	-	1·514
Potassium metaphosphate	+	-	-	1·465	-	1·483	-

Trimetaphosphoric acid solutions can be prepared by passing aqueous solutions of sodium trimetaphosphate through a cation exchange column in its hydrogen form.[6] Hydrolysis of sodium trimetaphosphate in aqueous solution leads ultimately to orthophosphate anions[5,22,37,68,80,81] the product being three molecules of monosodium dihydrogen orthophosphate,[68] with acid sodium triphosphate[61] and acid diphosphate as intermediates.[9,26,32] The rate depends markedly on the pH of the solution and on temperature: increasing hydrogen ion concentration and a rise of temperature from 70° to 100°C. sharply increase the rate of hydrolysis.[61] Hydrolysis to orthophosphate in neutral solution requires the solution to be boiled for several days,[37] and although the stability is less in acid solutions it is greater than that of most molecularly dehydrated phosphates under similar conditions.[81] Conductivity measurements indicate that the rate of hydrolysis bears no direct relationship to pH or to orthophosphate concentration,[5] but the general trends are illustrated by the following observations: in a 5·7N. and 5N. solution of hydrochloric acid at room temperature, a 0·51% solution of the trimer is 15 and 11·3% 'reverted' (*i.e.*, hydrolyzed to orthophosphate) within 5 minutes. In 0·8N. and 0·1N. acid, the same strength of trimetaphosphate is only 3·6 and 0·3% reverted, respectively, after 30 minutes. At pH 4·5 to 7, reversion is negligible at 37°C. even after 30 days, although up to 1·3% hydrolysis can occur within 7 hours on raising the temperature to 90°C. In similar solutions, at 37°C., 5N. and 1N. sodium hydroxide concentrations cause, respectively, 6•4 and 1•4% hydrolysis after two weeks, while at 90°C., 31•4 and 9•1% reversion occurs after 5 hours. These rates are smaller than those for pyrophosphate.[80] The presence of lanthanum, aluminium[80] and calcium[81] increases the rate of hydrolysis, but magnesium has little or no effect.[80,81]

In Table XXX are given rate constants for the hydrolysis of 0•1N. sodium trimetaphosphate in 0•1N. sodium hydroxide solution.[43,82] Controlled hydrolysis of the salt with sodium hydroxide in concentrated solution at room temperature results in the crystallization of sodium triphosphate hexahydrate after several hours.[83,84] The rate of triphosphate hydrolysis is also greatly increased at higher temperatures,[44] and care must be exercised in preventing further reversion of the triphosphate.[61] This can be achieved by adding a zinc salt to the reaction mixture, when the double salt, $Na_3ZnP_3O_{10},9H_2O$, readily crystallizes and takes no further part in the reaction.[21,22] Similar results are obtained in acid solution, where again the triphosphate hydrolysis can be arrested by addition of zinc ions.

TABLE XXX. - RATE CONSTANTS FOR HYDROLYSIS OF SODIUM TRIMETAPHOSPHATE BY SODIUM HYDROXIDE

Temperature (°C.)	Rate constant k(min.$^{-1}$)
65	0•010
75	0•022
85	0•042
90	0•077
Derived activation energy, E, = 20•0 kg.-cal./mole	

The hydrolysis is proton catalyzed and is of first order, with an activation energy of 19•9 or 20•0 kg.-cal./mole.[43,82]

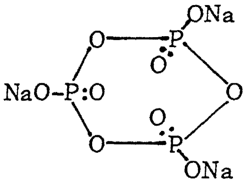
Other cations react as follows with sodium trimetaphosphate in aqueous solution:- silver nitrate gives a crystalline product;[73] calcium chloride in neutral solution gives no definite precipitate, but in alkaline solution a precipitate containing a phosphorus pentoxide to calcium ratio of 2:1 is obtained and this, on ignition at 700°C., yields a calcium pyrophosphate;[85] similarly, no precipitate is obtained with barium chloride, in contrast to linear poly- and polymeta-phosphates.[61,86] Inability to dissolve calcium soaps is taken to indicate that sodium trimetaphosphates form no complexes with calcium,[87] but measurements of the solubility of calcium iodate in solutions of the trimer do indicate complex formation and show[6] that the dissociation constant of the ionization $CaP_3O_9{}' \rightleftharpoons Ca^{\cdot\cdot} + P_3O_9{}'''$ is $3{\cdot}3 \times 10^{-4}$. In fairly dilute solutions neither zinc nor silver ions give a precipitate with sodium trimetaphosphate. The lack of precipitate with barium ions, and with ammonium molybdate, has been employed in an analytical separation scheme[41] and the failure to give a precipitate with silver ions is recognized as a measure of freedom from, especially, sodium hexametaphosphate.[6,41] The reaction with complex ferric thiocyanate shows no complex formation.[88] Polarography indicates that cupric and cadmium ions form no complex ions with the trimer, that zinc, manganese and lead form unstable complexes, and that ferrous ions form a stable complex compound.[89] Conductivity measurements, however, show the existence of ions of the type $MP_3O_9{}'$ when the divalent ion $M^{\cdot\cdot}$ is added to a solution of the trimer; when M is Ca, Ba, Mg, Mn and Ni, the dissociation constants of the ionization $MP_3O_9{}' \rightleftharpoons M^{\cdot\cdot} + P_3O_9{}'''$ are[90] respectively ($\times 10^{-4}$) 3•6, 4•5, 4•9, 2•7 and 6•0. The salt forms no precipitate with simple organic bases, in contrast to highly polymeric metaphosphates.[91] An impure form, once claimed to be the monomer, gives crystalline precipitates with silver, lead, mercury and bismuth nitrates in 0·3M. solution, amorphous precipitates with zinc, cadmium, cobalt, nickel and copper and no precipitate with magnesium and ammonium ions: an ammonium salt can be made from the lead compound by treatment with ammonium sulphide.[8] An unstable double compound, $Na_3P_3O_9,H_2O_2$, has been prepared from the constituent compounds.[15]

If an intimate mixture of sodium trimetaphosphate with sodium fluoride is heated at 800°C. for 6 minutes, carefully cooled and then leached with water and precipitated with ethanol, an 80% yield of sodium monofluorophosphate is obtained:-[44]

$$Na_3P_3O_9 + 3NaF \rightarrow 3Na_2PO_3F.$$

Other metaphosphates can be used in this reaction, but only the trimer is favoured since it can readily be obtained in the highly anhydrous state required to obtain good yields. The product, Na_2PO_3F, has been described fully.

The only possible structure that is in accord with the described preparation and properties is a cyclic structure of the type:-[22,60,92]



and this is most likely to be planar.[72]

No completely satisfactory method of analysis for the salt is known: a rough measure of its contribution to a mixture of sodium phosphates may be obtained by controlled hydrolysis to sodium triphosphate which can be determined by known methods.[44] The trimer can be identified by its optical properties.[44,68]

Sodium Tetrametaphosphate

Preparation.

Some claims,[78,79] based on conductivity evidence, for the formation of sodium tetrametaphosphate during the thermal conversion of the trimer into molten polymeric salts have been refuted.[5,36,42,49] The early method[3,93] (Mellor, II,869) of heating copper oxide with phosphoric acid at 100°C. for 2 hours and then at 450°C. for 24 hours, giving copper tetrametaphosphate, to which is added sodium sulphide to give a solution of the sodium tetrametaphosphate, has been shown to be satisfactory.[6,46,50,94] The salt is isolated as its decahydrate by precipitation with ethanol, but it has been pointed out that other metaphosphates may be present in the product.[10,22] This preparation has been shown to be identical with that obtained by a convenient and illuminating method which employs the controlled hydrolysis of the α- (volatile) form of phosphorus pentoxide, P_4O_{10}, (50g.) with water (300ml.) below 15°C. The solution is neutralized with sodium hydroxide, carbonate or bicarbonate: crystals of the decahydrate form on standing below 25°C., particularly if salted out with sodium chloride, to give a 60 to 65% yield.[21,22,43,56,95] This method is instructive in the elucidation of the structure of the tetrametaphosphate anion: the hexagonal α-phosphorus pentoxide is the dimer, P_4O_{10}, with a structure shown in Fig. 11. Hydrolysis can occur at any P-O-P bridge to give $H_2P_4O_{11}$ which can then hydrolyze further leaving an 8-membered cyclic system of tetrametaphosphoric acid, $H_4P_4O_{12}$.

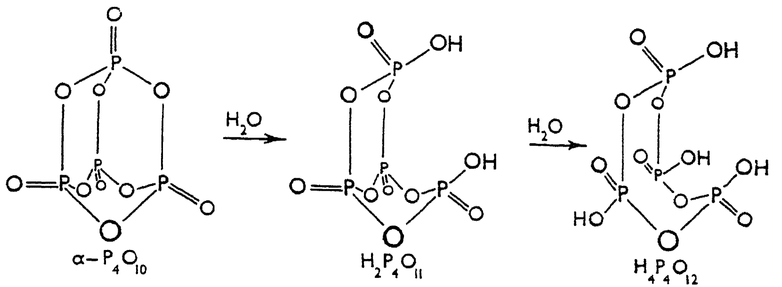


FIG. 11. DIAGRAMMATIC REPRESENTATION OF THE HYDROLYSIS OF α-PHOSPHORUS PENTOXIDE

The tetrahydrate, which exists in two forms, and the anhydrous salt are prepared by heating the decahydrate successively to 40°, 54° and 100°C.,[56] and the anhydrous salt can be reconverted to the tetrahydrate by treatment with sodium sulphate solution[18] and to the decahydrate by treatment with water below 25°C.[56]

An acid sodium tetrametaphosphate is said to be formed when sodium dihydrogen orthophosphate and phosphoric acid are heated to 300°C.:-[96]

$$2NaH_2PO_4 + 2H_3PO_4 \rightarrow Na_2H_2(PO_3)_4 + 4H_2O.$$

Separations of the salt are normally based on its solubility in water, but small-scale separations have been achieved by paper chromatography[11,63-66] by electrophoresis[97] and by ion exchange.[46]

Physical Properties.

Two forms of the tetrahydrate have been recognized:[56] a low-temperature form obtained on the immediate dehydration of the decahydrate at 40°, and a high temperature form obtained from the low-temperature form on heating to 54°C. The reverse transformation is not realized on cooling. The two forms are distinguishable by *X*-ray diffraction, and their discovery has clarified certain *X*-ray disagreements in the earlier literature.[56] The anhydrous salt is monoclinic, with cell dimensions $a = 9{\cdot}65$, $b = 12{\cdot}32$, $c = 6{\cdot}17$ with $\beta = 92° 30'$, the unit cell containing 8 metaphosphate groups.[46] *X*-Ray studies have shown that the structure is similar both in solution and in the solid state[66] and differs from that of the trimetaphosphate;[94] details of the *X*-ray characteristics of the acid salt have been given.[96]

Optical data are given in Table XXXI,[56] and infra-red absorption characteristics in Table XXXII.[70] The Raman spectrum shows a main frequency of 1154 cm.$^{-1}$ ($\omega_S(PO_2)$) and frequencies of 1244 and 660 cm.$^{-1}$, similar to those of the trimetaphosphates.[71]

TABLE XXXI. - OPTICAL DATA FOR SODIUM TETRAMETAPHOSPHATE

Salt	α	β	γ
Decahydrate	1·420	1·424	1·436
Tetrahydrate, low temp. form	1·441	1·459	1·472
Tetrahydrate, high temp. form	1·438	1·459	1·468

The density of the anhydrous salt has been given[46] as 2·18g./cm.^{3}, and the melting point of disodium dihydrogen tetrametaphosphate as approximately 400°C.[96]

The molecular weight has been confirmed as 415 ($Na_4P_4O_{12}$ = 408) by cryoscopy in water[4] and at the sodium sulphate decahydrate eutectic.[56,94] Conductivity measurements, a selection of which is given in Table XXXIII,

TABLE XXXII. - INFRA-RED ABSORPTION BANDS OF SODIUM TETRAMETAPHOSPHATE

$Na_4P_4O_{12}$		$Na_4P_4O_{12}, 4H_2O$	
Wave number (cm.$^{-1}$)	Intensity	Wave number (cm.$^{-1}$)	Intensity
1306	strong	3580	weak
1282	strong	3480	medium
1270	strong	3330	medium
1173	very weak	1693	weak
1125	very strong	1655	medium
1093	medium	1290	very strong
1037	very strong, broad	1266	very strong
to 991	very strong, broad	1122	very strong
882	very weak, broad	1109	very strong
794	medium	998	very strong, very broad
710	medium	880	very weak(?)
		748	medium
		697	medium

$Na_4P_4O_{12}, 4H_2O$ (metastable)	
Wave number (cm.$^{-1}$)	Intensity
3580	weak
3475	medium
3330	very, very weak
1670	weak
1622	weak
1284	very strong
1265	very strong
1117	very strong, sharp
1109	very strong
988	very strong, very broad
880	very weak(?)
750	medium
697	medium

TABLE XXXIII. - CONDUCTIVITY OF SODIUM TETRAMETAPHOSPHATE SOLUTIONS AT 25°C.[6]

Equivalent concentration	Equivalent conductivity
0·00010537	137·18
0·00022324	135·65
0·00041940	133·81
0·00056795	131·98
0·00077967	129·85
0·0011094	127·09
0·0014364	124·85
0·0021068	121·09

show that the salt is a 1:4-valent type, with Λ_0 143·80, of which 93·69 is contributed by the tetrametaphosphate anion.[6] A value of 70·27 has been assigned to the NaP_4O_{12}''' anion and the dissociation constant of the ionization, $NaP_4O_{12}''' \rightleftharpoons Na^{\cdot} + P_4O_{12}''''$, has been given as 0·009.[6] The ring structure displays an unsuitable geometrical pattern for adsorption on calcite so that calcium carbonate deposition is not inhibited in the presence of the salt; in contrast to the long-chain polymetaphosphates.[76,77] R_f values have been given inTable VII.[65](see page 1272).

Chemical Properties.

Thermally sodium tetrametaphosphate is not very stable, and at 375°C. passes gradually into sodium trimetaphosphate, the change becoming appreciable at 400°C. and fairly rapid at 500°C. and above.[56,79,94] At 410°, to 440°C. one of the insoluble sodium metaphosphates, presumably $NaPO_3$-II, is probably an intermediate.[50] An exothermic change has been recognized by means of heating curves at 400° to 450°C.[56] Heating the decahydrate leads successively to the tetrahydrate-low temperature form, to the tetrahydrate-high temperature form, and then to the anhydrous salt, at 40°, 54° and 100°C. respectively.[56] No other chemical changes appear to occur.

Tetrametaphosphoric acid solutions have been prepared by passing the sodium salt solution through an ion-exchange resin in its hydrogen form.[6] Hydrolysis of sodium tetrametaphosphate leads ultimately to orthophosphate with the probable intermediate formation of two molecules of pyrophosphate.[21,63,98] Rates of hydrolysis in 0·1N. acid and in 0·1N. alkali solutions are given in Table XXXIV. Calcium ions tend to increase the rate of hydrolysis, but magnesium has no effect.[81] Evidence has been obtained for the production of sodium tetraphosphate by hydrolysis of sodium tetrametaphosphate with a 100% excess of sodium hydroxide at 25° to 28°C.[21,63,98] Sodium triphosphate is therefore likely to be a further intermediate during complete degradation.[21,63] Hydrolysis during dehydration of the hydrates is negligible.[22]

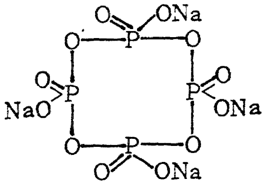
TABLE XXXIV. - HYDROLYSIS RATE DATA FOR SODIUM TETRAMETAPHOSPHATE[43,82]

Temperature (°C.)	Rate constant, k(min.$^{-1}$), in solutions of:-	
	0·1N. acid	0·1N. alkali
60	0·0018	-
65	0·0055	-
75	0·012	0·0012,[82] 0·0015
85	0·034	0·0029
90	-	0·0048
95	-	0·012,[82] 0·010
100	-	0·016
Activation energy (kg.-cal./mole)	25·3	26·8,[82] 26·0

Initial solutions are 0·1N. with respect to the tetrametaphosphate

Sodium tetrametaphosphate forms no precipitates with barium ions in neutral solution, in contrast to the soluble polymetaphosphates.[86] Ions of the type MP_4O_{12}'' are formed, however, with the divalent ion $M^{\cdot\cdot}$: from conductivity measurements, when M is Ca, Ba, Mg, Mn and Ni, the respective dissociation constants of the ionization $MP_4O_{12}'' \rightleftharpoons M^{\cdot\cdot} + P_4O_{12}''''$ are ($\times 10^{-6}$) 3·8, 10·3, 6·7, 1·8 and 11·3.[95] For the reactions $Ca_2P_4O_{12} \rightleftharpoons CaP_4O_{12}'' + Ca^{\cdot\cdot}$ and $CaP_4O_{12}'' \rightleftharpoons Ca^{\cdot\cdot} + P_4O_{12}''''$ the dissociation constants of $2{\cdot}2 \times 10^{-3}$ and $1{\cdot}3 \times 10^{-5}$ were respectively found from solubility measurements on calcium iodate in aqueous solutions of the salt.[6] Calcium soaps are not dissolved by the salt so that the stability of the complexes is not sufficiently high to outweigh the low solubility products of the soaps.[87] The salts $Na_3[FeCl_2(PO_3)_4]$ and $Fe[FeCl_2(PO_3)_4]$ have been isolated as light rose-coloured powders after the action of ferric chloride on a solution of sodium tetrametaphosphate;[88] evidence has also been obtained[10] potentiometrically for the existence of the complex ion $[FeCl_2(PO_3)_4]'''$. No addition compound of the tetramer with hydrogen peroxide has been isolated.[15] By potentiometry, tetrametaphosphoric acid is found to be tetrabasic with k_1 2·5 × 10^{-3}, k_3 6 × 10^{-9}, both well defined, k_2 4 × 10^{-7} and k_4 4 × 10^{-12}, both weak.[88]

The most reasonable structure to be assigned to sodium tetrametaphosphate is, in its simplest form:-



which is in agreement with the facts cited above.

Sodium Polymetaphosphates

1. 'Insoluble' Sodium Metaphosphates, $NaPO_3$-II and $NaPO_3$-III (Maddrell salts)

By heating disodium dihydrogen diphosphate, prepared thermally from sodium dihydrogen orthophosphate or a mixture of disodium hydrogen orthophosphate with ammonium nitrate, a mixture of sodium metaphosphates is produced, their formation becoming appreciable at 240°C. and rapid at 260° and above. Up to the melting point of 628°C., some sodium trimetaphosphate is also formed, its proportion becoming greater as the temperature rises until it is the sole product above 500°C. At lower temperatures, however, two insoluble forms of sodium metaphosphate predominate, type III at 250° to 280°C., and the high temperature form, type II at 300° to 400°C. Neither is formed below 200°C., and one attempt[69] to produce type III was not successful. At intermediate temperatures corresponding mixtures of types II and III with admixed trimetaphosphate are produced. The insoluble metaphosphates are readily isolated by cooling and extracting the soluble trimetaphosphate with water: this also serves to remove any unchanged acid pyrophosphate. Yields as high as 96% of type II can be obtained.[10,17,19,22,36-38,42,47-49,53,54,99-103] The transformations observed with increasing temperature are said to be irreversible.[22,42,47,49] The properties of the products are to some extent dependent on atmospheric moisture as well as on temperature, and a claim has been made that a soluble form of sodium metaphosphate is formed at 305°C. in moist air[104] but this has been contradicted in that the formation of the insoluble type II is favoured in the presence of steam at 300°C.[38] The low temperature form, type III, invariably contains large proportions of trimer (or dimer?) and of acid pyrophosphate, and this probably led to the claim that the low temperature form was in fact an insoluble form of the trimer.[36,37] The dissociation pressures of the thermal dehydration of disodium dihydrogen diphosphate have been given in Table XX[105] (see page 1300).

Heating sodium tetra-ammonium triphosphate at 200°C. causes loss of ammonia and water with formation of insoluble sodium metaphosphates in 70% yields, together with other polymetaphosphates.[60] Similarly, heating sodium ammonium hydrogen orthophosphate gives disodium ammonium orthophosphate at 220°C., and at 320°C. this loses ammonia and reverts to a sodium metaphosphate hemihydrate which may be a type II or III derivative.[106] The insoluble form, presumably type II, is also said to be formed irreversibly on heating sodium tetrametaphosphate at 410°C.,[50] or the Kurrol (type-IV) polymetaphosphates at 380° to 490°C.,[55] and there is one report[42] of a similar conversion of sodium trimetaphosphate at 400°C. or above. Heating sodium hydrogen alkyl orthophosphates possibly gives the Kurrol salts, which are distinct from types II and III.[48]

The insoluble sodium metaphosphates, probably mainly type II, have found use in dentifrices,[100,107] in polishing agents[101] and abrasive detergents[102] and in powders used for lubricating rubber gloves.[103] Despite its relatively low solubility the insoluble metaphosphate II has been suggested as a stable calcium-sequestering agent in water softening.[108]

Type II and type III are distinguishable by X-ray powder techniques,[1,10,36,37,53] although it has been stated that type III has an X-ray pattern indistinguishable from that of sodium trimetaphosphate[36] and is therefore largely a polymorph of the trimer. For the Maddrell salt (type II?) the following crystallographic details have been given: $a = 15{\cdot}30$, $b = 6{\cdot}96$, $c = 7{\cdot}05$, $\beta = 93{\cdot}3^\circ$, $z = 12$,[109] and the salt is monoclinic. For both classes, II and III, N_g is 1·525 and N_p is[53] 1·502 with $2V$ 78°, α 1·498, β 1·510, γ 1·529, the crystals being biaxial positive and orthorhombic(?).[53,68,69] Infra-red techniques have also been applied to the salts,[10,70] with the results given in Table XXXV.[70] Monocrystal diagrams of type II, of meta-arsenatophosphates,[55] sodium polymeta-arsenates and of monoclinic β-wollastonite are very similar: each is of the chain unit type and is readily cleavable along the b axis.[110]

TABLE XXXV.-INFRA-RED ABSORPTION BANDS OF SODIUM METAPHOSPHATE II AND III

$NaPO_3$-II		$NaPO_3$-III	
Wave number (cm.$^{-1}$)	Intensity	Wave number (cm.$^{-1}$)	Intensity
~1315	medium, sharp	~1315	medium, sharp
1298	very strong	1298	very strong
1160	medium	1160	medium
1104	strong	1104	strong
1097	strong	1097	strong
1060	strong	1060	-
878	very strong, very broad	867	very strong, very broad
742	weak	742	weak
719	medium	719	medium
702	medium	702	medium

The salt undergoes a transition, indicated conductimetrically, in the range 600° to 650°C., as compared with that of sodium dihydrogen orthophosphate at 400° to 600°C.[17] A specimen of undefined sodium metaphosphate, examined for heat capacity changes under adiabatic conditions, gave the following results:-

Temperature (°C.)	350	470–480	490–524(max.)	529	540–577
c_p(g.-cal./g.)	0·20	0·18	rising to 0·37	0·20	rising to 1·37

The transitions at 524° and 577°C. have, respectively, integral heats of 155 and 860 g.-cal./mole, and the transition at 524°C. is reversible.[111]

At 402°C., in a closed tube, type II consists of 0·93 weight fraction of the salt in water,[75] but under normal conditions less than 0·1g./l. of the type III(?) dissolves in water at 15°C.[47] Determinations of viscosity have been made on solutions prepared by treating types II and III with 5% aqueous ammonium chloride, in which they dissolve, and then reprecipitating with ethanol and dissolving the solid in water: despite probable depolymerization in this dissolution procedure, viscometric molecular weights of 10^6 were found.[112]

The insoluble metaphosphates, $NaPO_3$-II and -III, are also soluble in solutions of most alkali metal and ammonium salts, except those of sodium, including pyrophosphates and long-chain polymetaphosphates,[3,47] in which they give colloidal solutions of high viscosity,[3] and alkali metal soaps.[102] The insoluble metaphosphates are precipitated from these solutions with ethanol and the precipitate is found to dissolve in water to give highly viscous solutions of up to 1% strength; this viscosity is reduced to that of simple salt solutions when electrolytes are added or when the solution is heated for some time.[22] The effect of the alkali metal and ammonium salts is probably due to a process of base exchange with the highly polymeric metaphosphate chain system.[22]

When sodium metaphosphate type III is heated it passes into type II at 350° to 400°C. and the product then passes into sodium trimetaphosphate at 500° and above;[36,37,50] this in turn is converted into the polymeric melt at 625° to 628°C.[48,50] Even on extremely rapid heating conversion to the trimer is so rapid that the melting point is unaffected.[21,22] Alone, type III is said to pass into the trimer at 550°C. and type II into the trimer at 485°C.[38]

Continued boiling of the sodium polymetaphosphates with water ultimately leads to a solution of sodium dihydrogen orthophosphate,[37] but it is possible to isolate up to 53% of sodium trimetaphosphate in the hydrolysate: this, however, is no reason for supposing that the cyclic trimer structure forms part of the polymeric phosphate system.[55] Despite the low solubility of the salts, it is said that they possess good sequestering power for calcium ions, and in water treatment have some advantages over glassy polymetaphosphates owing to their greater resistance to hydrolysis.[108]

2. Sodium Hexametaphosphate', Graham's salt, 'glassy sodium metaphosphate'.

It has long been recognized that the sodium metaphosphate obtained on melting any sodium metaphosphate and then chilling the melt is not a true hexamer, but rather a mixture of high polymers which might, by chance, contain a very small proportion of hexamer depending on the conditions of heating and cooling. Nevertheless, some claims have been made for the preparation of a true crystalline sodium hexametaphosphate by one of the following methods: heating sodium ammonium orthophosphate tetrahydrate to 700°C. and rapidly quenching the melt;[3,7,113] heating a mixture of disodium hydrogen orthophosphate and ammonium nitrate at 270° to 280°C. for several days;[31,114] neutralizing hexametaphosphoric acid that has been prepared by the action of phosphorus pentoxide on ice-cold water,[27,88] the product being the decahydrate. The product is said to differ considerably from the glassy 'hexametaphosphate' but is readily converted into it. It is resistant to hydrolysis,[27,31,114] the half life at 55° to 100°C. being about 5 hours (cf. approximately 2 hours for Graham's salt) but conversion to polymetaphosphates is said to occur at a temperature 30° lower than that at which the trimer isomerizes.[27,31] The salt is said to form a precipitate, probably of $Na_2Pb_2(PO_3)_6$, with excess of lead ions in solution[7,113] and analogous precipitates with other heavy metal cations.[114] In smaller quantities the sulphates of lead, barium and strontium dissolve to form complexes of the type[113] $Na_4M(PO_3)_6$ and it is possible that $Na_2Ba_2(PO_3)_6$ and $Ba_3(PO_3)_6$ may also be formed;[115] analogous soluble complexes are formed with many other cations.[113] Complexes of the type $Na_3[Fe(PO_3)_6]$ are formed with cold ferric chloride or complex ferric thiocyanate; these insoluble products are decomposed in concentrated acid or alkali.[88] The hexametaphosphate anion has been postulated as having a ring structure, with three ionizing stages: k_1 10^{-2}, k_2 $2{\cdot}2 \times 10^{-6}$ and k_3 $1{\cdot}6 \times 10^{-8}$ [88,115] Much of this work is unsubstantiated and is based on material the identity of which may be in doubt owing to its method of preparation.

Preparation of Glassy Sodium Metaphosphate, Graham's salt.

The material popularly known as sodium hexametaphosphate is produced by heating any sodium metaphosphate (and, hence, sodium dihydrogen orthophosphate, disodium dihydrogen diphosphate or sodium ammonium hydrogen orthophosphate) above the melting point at 628° C.[6,21,22,26,27,41,44,48-51,78,79,86,94,116-124] Temperatures of 640° C.[49,79] and higher[6,41,44,116,120,122-124] have been recommended. Interaction of hydrochloric acid with an insoluble sodium metaphosphate may also produce Graham's salt[125] in solution. On a large scale, the 'hexametaphosphate' is prepared by heating the correct proportions of sodium carbonate and phosphoric acid to 1000° C.[26,118,121,124] or from sodium dihydrogen orthophosphate,[117,118,120,123,126] sometimes mixed with the dibasic orthophosphate and sodium carbonate,[119] from superphosphate, sodium sulphate and lime,[127] or from sodium chloride and phosphorus pentoxide.[32] In all cases the solid salt is obtained by rapidly chilling the melt to below 200° C., when a brittle transparent glass results without devitrification.[44,51,86,118,120,124] The product shows some variation with the moisture content of the reagents used and of the ambient atmosphere[22] and the commercial product is slightly hygroscopic.[26] On a large scale, purification is achieved by adjusting the conditions of dissolution of the reagents,[118,121] and by precipitation of impurities with sodium carbonate or hydroxide[128,129] or as orthophosphates or hydroxides. On a small scale, separations have been performed by paper chromatography[64-66] and electrophoretically,[97] or by precipitation with silver ions and treatment of the precipitate with sodium chloride.[6,41]

Uses.

Of all the metaphosphates, glassy sodium metaphosphate has found the greatest and most diversified uses in industry.[26,127,130-135] Because of its ability, in very low concentrations, to sequester calcium and magnesium ions and to be adsorbed on calcite, and because of its own surface-active properties, it has found application as a detergent and in detergent compositions,[26,40,117,125,126,136-161] in preventing the deposition of scale and of calcium and magnesium salts and in dissolving calcareous deposits, where its non-toxicity is an advantage,[26,162-189] and in mineral flotation.[190-192] The salt has found extensive application in corrosion control[26,77,120,159,171,193-207] and in the prevention of flocculation[208] of clays[209,210] and soils,[211] e.g., in drilling muds,[26] of blood and serum,[212] e.g., in abbattoirs,[26] and of inorganic salt crystals[213] such as ammonium nitrate[214] and lead arsenate.[215] In the food industry it has been used for treatment of alginate[216] and calcium pectinate[217] dispersions, as an antioxidant in stabilizing fatty compositions,[218-220] in refining fatty acid glycerides,[221] in improving whipped egg-white,[222] in decalcifying potato starch,[223] and for sequestering, especially, iron and calcium ions in the improvement of wines[224] and glues.[225] Spreading cheeses are made by adding the salt to normal cheese in order to liquefy the casein content.[26] In the leather industry, sodium hexametaphosphate glass has found use as a preventive of iron stains in tanning[226,227] and in chrome leather manufacture.[228-231] It is said that 100 million pounds of soap per year are saved in the United States alone by using the salt in the textile industry to prevent deposition of lime soaps[26,232,233] and staining due to calcium, magnesium, iron, copper, lead and manganese;[234-237] it is also used in the physical treatment of fibres.[238-241] Besides preventing undesirable calcium salt deposition, the salt improves the washing properties of photographic film.[242-244] It has been used as a constituent of glasses,[245] of jewelry[246] and refractory[26,247] compositions, of inorganic lubricants[248,249] and of paint-stripping compositions.[250] Liquid fuel can be recovered from 'solidified' fuels by means of the salt[215] which also has a stabilizing effect on hydrogen peroxide used for treatment of cellulose[252] and a catalytic effect in the condensation of phenol-formaldehyde resins.[253] Disodium dihydrogen pyrophosphate has been prepared from the salt by controlled hydrolysis.[32]

Physical Properties.

X-Radiograms of glassy sodium metaphosphate strongly indicate that the salt is not a hexamer and that the degree of polymerization is dependent on the temperature of preparation: this supposition is supported by dialysis, and by observations of cooling curves, conductivity and complex formation.[27] Drawn fibres of the salt show *X*-ray diffraction patterns similar to those of organic fibres but unlike those of drawn sodium silicates; they also display birefringence.[254] No difference is observed between structures in the solid and in solution, and there is some evidence for the existence of trimeric rings in the glass.[66] The refractive index has been given as 1·482,[44] and 1·4847.[69] The character of the salt has been studied microscopically.[68,73] Infra-red absorption characteristics are given in Table XXXVI.[70]

TABLE XXXVI.-INFRA-RED ABSORPTION BANDS OF GLASSY AND FIBROUS SODIUM POLYMETAPHOSPHATES

$(NaPO_3)_n$ glass		$(NaPO_3)_n$-IV fibrous	
Wave number (cm.$^{-1}$)	Intensity	Wave number (cm.$^{-1}$)	Intensity
1262	very strong, broad	~1630	weak, broad
1150	weak	1268	very strong, very broad
1083	strong, broad	1150	medium
980	medium, very broad	1110	strong
863	medium	to 1082	strong
770	very weak, very broad	996	strong, broad
to 700	very weak, very broad	869	very strong, broad
		778	weak
		724	weak
		698	medium

The Raman spectrum shows a main frequency of 1154, corresponding to $\omega_S(PO_2)$, and a frequency at 1244 cm.$^{-1}$ attributed to an asymmetric PO_2 vibration. All other frequencies are relatively diffuse.[71] The main frequency shifts only to 1159 cm.$^{-1}$ in solution and the Raman spectrum is markedly different from that of metaphosphoric acid.[255]

The melting point has been variously given as 608° to 630°C., but 627·6° or 628°C. appear to be the most generally accepted figures.[21,22,53,54,68,69,256] The lower limit of crystallization is approximately 280°C., corresponding to the beginning of softening and to a transformation point, shown by differential thermal analysis, found during heating. Maximum crystal development occurs at 440°C.[257] The density of the melt from 630° to 1000°C. is given by the expression $d = 2{\cdot}461 - 0{\cdot}000338t$, expanded to $d' = 2{\cdot}372 + 0{\cdot}089(Na_2O/P_2O_5) - 0{\cdot}000338t$ to take account of slight variations in the ratio of sodium to phosphorus. These data indicate a degree of polymerization of approximately 9 and give some support to a random reorganization hypothesis of structure.[258] The effect of pressure applied during cooling of the melt has been investigated.[259] The specific volume coefficient is $4{\cdot}3 \times 10^{-4}$ between 600° and 700°C.[260] Viscosity of the melt can be expressed by $\eta = 0{\cdot}0016e^{b/RT}$, where log *b* is 4·207 and *R* is in g.-cal./degree-mole, indicating[261] Newtonian flow and with a flow unit (degree of polymerization) of approximately 8. A similar expression, $\eta = kv^{-7/8}e^{B/RT}$, where v is specific volume and B and k are constants, has also been proposed.[262] The surface tension of the melts is given by the expression $\gamma = 218{\cdot}3 - 0{\cdot}0379t$.[258] The viscosity of sodium metaborate–sodium metaphosphate melts shows abnormal values which are attributed to colloid formation when 60% of metaborate is present; and when

38% of sodium metaborate is present the liquid assumes the character of a supercooled liquid having increasing viscosity with increasing temperature.[263] The system KPO_3–$NaPO_3$ has a eutectic at 535°C.[264] and a double compound, $3NaPO_3,KPO_3$, the optical properties of which have already been given in Table XXIX[52] (see page 1322). No exchange of phosphorus occurs between the glassy hexametaphosphate and the trimer at 0° and 25°C.[74]

The vitreous material is hygroscopic[26] but dissolves only slowly in water though, in time, it gives a highly concentrated solution;[6,21,22,44] solubility figures of 973·2g./l. at 20°C. and 1744g./l. at 80°C. have been recorded.[265] The solutions, on evaporation, give a thick syrup from which the glass can be recovered.[37] Solubility in organic solvents, including ethanol, is low, and the salt can be precipitated from aqueous solution by the addition of miscible organic solvents.[167] The density of aqueous solutions is given by the expression $d_4^{25} = 0{\cdot}99707 + 0{\cdot}078C$, where C is the equivalent concentration, up to a concentration of 0·35N.[6] The pH of a solution in water is dependent on the moisture content of the salt: the commercial material has a value of 5·5 to 6·8,[26,117] but may be much nearer 7 if the salt is completely free from water when made.[22] Cryoscopic measurements have indicated that formation of salts of the type $\{Na_2[Na_4(PO_3)_6]\}_n$ is possible[7] and that the degree of polymerization[266] of the glass is 4, but these suggestions are regarded with some reserve.[22] Viscometric data for the solutions may be represented by the expression $\eta_{sp}/c = \frac{A}{1+B\sqrt{c}} + D$, where A, B and D are parameters increasing with increasing molecular weight; the intrinsic viscosity, $A + D$, is proportional to $M^{1{\cdot}87}$, where M is the molecular weight, thus suggesting the presence of rod-like ions and no chain-branching at infinite dilution.[267] The viscosity of the solutions is abnormally high,[6] the specific viscosity coefficient of aqueous solutions increasing with increasing concentration, and it has been demonstrated viscometrically that the degree of polymerization of the salt decreases with increasing temperature (from 650° to 800°C.) of preparation; moreover the specific viscosity–temperature curves vary with the pH of the solution.[122] In the presence of tetramethylammonium bromide, solutions of the salt show a linear relationship between intrinsic viscosity and the number of phosphorus atoms in a polymeric metaphosphate chain:[268] $[\eta] = 1{\cdot}25 \times 10^{-5}M_V + 0{\cdot}085$, where M_V is the average viscometric molecular weight. The viscosity of freshly prepared aqueous solutions decreases over a period of 12 hours, which may be due to decomposition of minor quantities of branched polymers, and then remains fairly constant. In dilute sodium bromide solution, intrinsic viscosities are proportional to molecular weights determined by light-scattering methods.[269] A polymetaphosphate glass containing 62·5% of phosphorus pentoxide shows that, in water, the flow-units are water up to 20% concentrations of the phosphate, and above that figure the flow units are hydrated polymetaphosphate anions.[270]

Dialysis measurements indicate that the metaphosphate glass is highly polymeric (the sedimentation constant is $1{\cdot}5 \times 10^{-3}$ c.g.s. units)[271] although less so than the corresponding potassium compounds.[272] Light scattering in aqueous solutions has been studied[269] and flow birefringence measurements indicate the presence of long rod-like anions in aqueous solution: birefringence is not observed in lower polymers except in high concentration.[273] Conductivity data are given in Table XXXVII;[6] the property shows a positive pressure coefficient.[274] The conductivity measurements show that, as the molecular weight increases, the number of sodium ions associated with the anion also increases, the binding reaching 70% at a chain length of 150 phosphate units.[275] Conductivity data also show the absence of critical micelle formation concentrations above 5×10^{-6}N. solutions,[6] contrary to a suggestion

TABLE XXXVII. - CONDUCTIVITY DATA FOR GLASSY SODIUM POLYMETAPHOSPHATE

Equivalent concentration	Equivalent conductivity
0·000005641	87·8
0·000010084	84·3
0·000022507	77·4
0·000033125	73·0
0·000059768	64·05
0·000095087	59·30
0·00020159	52·19
0·00062650	42·57
0·0013768	37·64
0·0024519	34·46
0·0046007	31·49
0·0092287	29·83
0·019242	27·57
0·032249	26·56
0·064044	24·81

that associated hexameric units might exist in solution.[68]

The salt has been recovered unchanged from an ion-exchange column when orthophosphate and pyrophosphate have been strongly retained,[276] and activity measurements employing an ion-exchange technique indicate a degree of dissociation depending on chain length and falling in the sequence of cations: $K^{+}>Na^{+}>Li^{+}$.[277] Measurements of the solubility of calcium iodate in the presence of the salt are not amenable to ready theoretical treatment.[6] The glass has been separated in solution from other sodium phosphates by paper chromatography:[64,65] in most solvents the R_f value is zero (see Table VII, page 1272), although it is said to vary with the molecular weight of the anion.

The effect of glassy sodium polymetaphosphate in stabilizing montmorillonite soils,[278] on the staining and tanning of collagen,[279] in dispersing clays[280] and in peptizing Prussian Blue[281] has been largely explained on the basis of polyanion adsorption phenomena. The salt increases the viscosity of potato starch pastes,[282] improves the crystal size of ammonium chloride during crystallization from water,[283] lowers mullite formation in refractories[247] and hinders the formation of fibrous sodium polymetaphosphate.[48] The effect of the glassy metaphosphate on the particle size of kaolin,[284] on soils[211] and on the ζ-potentials of certain solids[285,286] has been investigated. Traces of uranium in the fused salt are said to render it luminescent when activated optically or cathodically, but not by X-rays.[287] Mutarotation of glucose is less in Graham's salt solutions than in tetrasodium pyrophosphate and sodium dihydrogen orthophosphate solutions.[288] The sinking times of cotton in solutions of the salt have been measured.[150]

Chemical Properties.

When glassy sodium polymetaphosphate is in a fairly pure state, one of the most striking reactions of its melt is its conversion, on cooling, into other sodium metaphosphates. The rapid chilling of the melt to give the glassy variety has already been described under the preparation of Graham's salt. But other varieties of the product are known.

(*a*) The molten salt has a strong affinity for water and even at 630°C. the melt can absorb up to approximately 1% of water from the surrounding atmosphere if this is not dry. It appears that at least some of this water is combined, and the solid obtained after chilling when made up as a 1% solution in water has a pH of[117] 5·5 or 5·7. This solution is apparently a true solution, in contrast to a solution prepared from a melt that has been chilled after drawing dry air over it at 700°C. for 24 hours. The latter dried vitreous material dissolves by a process of swelling to give a colloidal solution with a pH of 6·5 to 7. It has been pointed out[44] that it is unlikely that under normal laboratory or commercial conditions the glassy product can be obtained with a purity greater than 95%, the balance being acid polyphosphates formed by hydrolysis by the trace of water present.[22] Unfortunately most of the physico-chemical work on glassy sodium metaphosphate has been performed on the moist material, typical percentage compositions of which are as follows:-

	Laboratory[289]	Commercial[289]	Commercial[26]
Trisodium orthophosphate	0·3	1·0	-
Sodium triphosphate	9·0	28·0	30
Sodium 'hexametaphosphate'	90·0	72·0	70
Total phosphorus	30·4	29·3	-

(*b*) Tempering of the melt at 575° to 625°C.[18,36,37,44,51,52] gives rise to sodium trimetaphosphate ($NaPO_3$-I) in high yield. If the melt contains a trace of water, the conversion to the trimer seems to be favoured, and, during the formation of the trimer, steam may be suddenly and vigorously expelled. Polymorphs $NaPO_3$-I′ and -I″ are prepared by controlled cooling to 500° to 525° and 375° to 525°C. respectively.[54]

(*c*) If the melt is cooled moderately slowly to 550°C. and gently reheated, especially if the melt is nucleated with Kurrol salt, silica, carborundum or insoluble sodium metaphosphate type II, a small proportion of brittle fibrous sodium polymetaphosphate (Kurrol salt, $NaPO_3$-IV) may result.[22,47,48,54,55,108] The preparation is capricious and is usually accompanied by formation of much sodium trimetaphosphate and glassy sodium polymetaphosphate, both of which, however, are readily separated because of their high solubility in water.

The system $NaPO_3$–$Na_4P_2O_7$ has been examined in some detail. Although the possibility of existence of higher sodium polymetaphosphates[290] at high temperatures[68,291] is not completely excluded, it appears that the products obtained by cooling the melt are usually mixtures of sodium polymetaphosphate or tetrasodium pyrophosphate with sodium triphosphate; the latter can be obtained almost exclusively when the reagents are in equimolecular proportions and the melt is cooled slowly enough. In such cases the product is sodium triphosphate type I, which can be converted into type II by very slow cooling to just below 450°C., or by converting to the hexahydrate and thermally dehydrating this salt.[21,22,53,68,69,291-294] The system has a eutectic at 552°C. which contains 0·31 weight fraction of tetrasodium pyrophosphate, and at the peritectic at 622°C. the liquid contains 0·495 weight fraction of the pyrophosphate.[53,68,69] Details are given in Fig. 8. (see page 1294).

Colours due to cobalt, nickel or copper salts dissolved in molten sodium polymetaphosphate in the presence of a little sodium carbonate may possibly be caused by the formation of sodium triphosphates.[295]

Reduction of the molten salt with finely divided carbon at 1200°C. gives rise to a yellow solid distillate; this material has the character of a mixture of phosphorus and phosphides.[296] During electrolysis of the melt the cathode reactions may be represented by:-[297]

$$5Na + NaPO_3 \rightarrow P + 3Na_2O \text{ and}$$
$$Na_2O + NaPO_3 \rightarrow Na_3PO_4$$

and the anode reaction by:-

$$4PO_3 \rightarrow 2P_2O_5 + O_2$$

Fusion of the melt with sodium hydroxide is said to give sodium tetraphosphate,[298] but the product is probably a mixture of sodium phosphates. Electrolysis of metal salts dissolved in molten sodium polymetaphosphate has been described.[299]

Details have already been given of the double compound $3NaPO_3,KPO_3$ which is formed in fused mixtures of the constituent salts.[52] Some optical properties of this compound are given in Table XXIX. In the system $(NaPO_3)_n$-$(Ca(PO_3)_2)_m$, a double compound $[4NaPO_3,Ca(PO_3)_2]_x$, congruent m.p. 738°C., has been discovered; it is biaxial negative, with $2V$ 80°, α 1·518, β 1·564 and γ 1·581, forming a eutectic with 0·99 weight fraction of sodium metaphosphate at 625°C. and with calcium metaphosphate (0·46 weight fraction) at 725°C.[256] With barium titanate, a eutectic containing 0·7% of barium titanate is formed at the m.p., 580°C.; the metaphosphate is a poor solvent for the titanate even at 1000°C.[300] The glasses formed from lead, cadmium and manganese oxides with molten sodium polymetaphosphate have been described.[301] Molybdenum and tungstic oxides dissolve readily in the molten salt to give the following equilibrium diagram maxima or minima: (i) MoO_3; 540°C. (25% sodium metaphosphate), and 320°C. (both min.) and 600°C. ($NaPO_3,MoO_3$, max.): (ii) WO_3; 350°C. (30% sodium metaphosphate, min.) and 850°C. ($NaPO_3,WO_3$, max.). The double compound $NaPO_3,MoO_3$ is soluble in hot water giving a solution which has typical orthophosphate properties.[302] With sodium pyroarsenate, sodium metaphosphate shows no maxima in the freezing-point curves, and no double compounds; a minimum, possibly a eutectic, is found at a composition of 82% of sodium metaphosphate.[303] Insoluble double compounds with ferric oxide, $2NaPO_3,Fe_2O_3$, and aluminium oxide, $2NaPO_3,Al_2O_3$, are formed, with sodium dichromate, by heating an aqueous mixture of chromium metal or compound with an iron (or aluminium) compound at 250°C. under pressure in the presence of phosphorus or an alloy or compound of it.[304]

Depolymerization during passage of a solution of glassy sodium polymetaphosphate through an ion-exchange column (Amberlite IR-100H) is slight, but the acid eluate after 24 hours is considerably depolymerized on the evidence of paper chromatography.[305] The glassy metaphosphates are slowly hydrolyzed in aqueous solution,[265] although a cold neutral solution can be kept for some days and possibly weeks without serious decomposition.[138] Increasing temperature markedly increases the rate of hydrolysis[26,61,138,217,265,306,307] as do small concentrations (1 to 2%) of sodium carbonate or hydroxide;[26] the rate is much greater in acid solutions, falling abruptly with increasing pH and reaching a maximum stability to hydrolysis at pH 10.[81,138,217,265.306] In these solutions the rate of hydrolysis is increased by the presence of calcium ions, but magnesium ions have no effect in low concentrations,[81] and pyrophosphate does not appear to be a product in the reaction.[13] There is, however, some indirect evidence for[9] the intermediate formation of pyrophosphate during complete breakdown to the ultimate product, sodium orthophosphate.[61,68,138,140,166,306] Hydrolysis to orthophosphate is a necessary step prior to determination of metaphosphate indirectly as, e.g., magnesium pyrophosphate: nitric acid is a suitable hydrolytic medium.[41,44,289] The reaction is of first order, and appears to be inhibited by the presence of orthophosphate.[13] Sodium hydroxide, especially in increasing concentration, causes breakdown to other metaphosphates[44,138,265] before forming a mixture of sodium orthophosphate and pyrophosphate when 0·5 to 2N. sodium hydroxide is used.[308] The action of magnesium and calcium ions during hydrolysis by sodium carbonate leads to greatly increased rates, but not during acid (sodium dihydrogen orthophosphate) hydrolysis.[22] The half life of the vitreous sodium polymetaphosphate in N/16 aqueous solution is approximately 2 hours at 55° to 100°C., the rate being somewhat dependent on the time and temperature of heating during the preparation of the metaphosphate;[31] the resulting solution is weakly acid. The following rate constants in aqueous solution have been reported:[307] 100°C., k 1·75; 60°C., k 0·0228; 45°C., k 0·0034. Comparative rates of hydrolysis of the salt and of sodium triphosphate are given in Fig. 10. (see page 1307).

The controlled alkaline hydrolysis in dilute solution at 70° to 100°C. that leads to a 6 to 1 mixture of ortho- and trimeta-phosphates[61] (and hence to triphosphate) is of interest in the elucidation of the structure of polymetaphosphates. It might be possible to envisage trimetaphosphate rings in the polymer, but a distinctly separate step of isomerization during hydrolysis seems more likely.[22,61] Typical hydrolysis data for the commercial material (Calgon) have been given.[26,61] Enzymic hydrolysis has also been studied: at 38°C., yeast phosphatase shows a maximum effect at pH 4·2.[309]

Two-dimensional paper chromatography affords some evidence for the formation of tri, tetra- and possibly penta- and up to at least octa-metaphosphates of a cyclic nature, together with long-chain polyphosphates, in partially hydrolyzed glassy sodium polymetaphosphate solutions: hydrolysis appears to proceed by stepwise elimination of end-groups.[310,311]

The pH of an aqueous solution varies with the moisture content of the glass as prepared. Values of 5·5 to 5·7 for the moist glass[22,117] and[22] 6·5 to 7 for the dried material have been quoted. Solutions, when titrated with strong acids and bases, behave like those of a salt of a fairly strong acid, with a single inflexion point at pH 7,[22,27,92] (see Fig. 7, page 1292). If the acidity of the 'moist' material is assumed to be due to end-group acidity, molecular size can be calculated,[312] but the acidity may be due to acid polyphosphates.[22]

The reactions of sodium polymetaphosphate glass with organic amino compounds to give microscopically recognizable products has been described.[73,91,313] The possible combination of the salt with protein in leather either by combination with carbonyl end-groups, or with amino groups or by electrostatic attraction has been discussed in relation to the tanning of leather in presence of the salt.[228] Reaction with collagen[314] and serum and plasma proteins[315] has also been examined. Actinomycin forms no complexes with sodium polymetaphosphate glass unless magnesium ions are present.[316]

The ability of vitreous sodium polymetaphosphate to sequester several cations, especially the alkaline earths, is of considerable commercial interest. It has long been recognized, however, that far less than that required for complex formation is sufficient to prevent calcium salt scale formation. A 'threshold' treatment with as little as[142,164,166] 0·5 to 2 or 2 to 4 p.p.m.[169,174,176] of 'hexa' will prevent deposition of calcium carbonate in municipal water supply equipment or in oil-field and cyanidation processes, and 1 to 5 p.p.m.[164,165] will serve in cooling systems of internal combustion engines when the feed waters contain 150 to 300 p.p.m. of calcium carbonate. Five to 10 p.p.m. of the salt may be required to prevent deposition of other calcium, barium and strontium salts.[176] In these respects, the salt is several times more effective than sodium pyrophosphate[118,162,307] but roughly equivalent to sodium triphosphate[178,307,317] (306 p.p.m. were required to prevent 100 p.p.m. of calcium carbonate precipitating compared with 800 and 417 p.p.m. of pyro- and tri-phosphate, in an empirical test[307]). The effect is reduced with increasing temperature. A measure of the activity of a solution can be made by titrating with a standard barium or calcium solution to the appearance of an opalescence or by finding the quantity of gypsum retained in solution,[40,118,140,307] but it has been pointed out that the methods cannot be satisfactory owing to their high sensitivity to temperature and pH of the solution.[68] Prevention or postponement of precipitation of alkaline earth sulphates,[174,318,319] calcium oleate,[142,146,320] phosphate[162] and oxalate[40] can also be achieved. High concentrations or large excesses of soluble salts will, however, cause precipitation of metal 'hexametaphosphates';[41,86,321] even calcium carbonate might precipitate under these conditions,[322] and the sequestering power certainly decreases at higher concentrations.[323] Precipitation with silver ions serves as a delicate test for sodium polymetaphosphate, for example in sodium trimetaphosphate,[6] and precipitation with barium ions as $[Ba(PO_3)_2]_x$[321] is used in the separation of polymetaphosphate from most other sodium phosphates.[41] The precipitate is ultimately hydrolyzed by means of nitric acid and the orthophosphate determined by standard methods.[41,289]

When precipitation does occur after delay, the crystals of alkaline earth carbonates are abnormally large.[324] Precipitated salts such as calcium sulphate[265] and carbonate,[142,164,265] barium and magnesium carbonates,[265] calcium phosphate,[162] calcium soaps[87,140,178,317] and calcium pectinate[217] are slowly dissolved in low concentrations of sodium polymetaphosphate in water, but the efficiency of the ambient solution in *preventing* precipitation is thereby markedly reduced, presumably owing to adsorption of the phosphate on the salt surfaces.[142] The effects of pH and temperature on the precipitation and dissolution of these salts have been examined in detail.[87,317] All the effects of threshold treatment appear to be little changed by the presence of relatively large concentrations of sodium chloride or sulphate in the solution,[142] but ions which precipitate calcium weaken the activity of the phosphate.[323] Similar sequestering properties for iron and manganese have been observed.[176,227,325]

Although sequestration[140] may play an important part in the initial stages of the dissolution of scale and other kindred precipitates, it is not sufficient to account for the prevention of precipitation at the threshold concentrations. In this connexion, it has been observed that the ζ-potential of pure Iceland spar is reduced from approximately -18mV. to -60mV. by as little as 2 to 4 millimole/l. of glassy sodium hexametaphosphate, whereas sodium nitrate and disodium hydrogen orthophosphate reduce it by only 2 and 10mV. respectively at the same concentrations.[286] This is in agreement with the fact that the polymetaphosphate chain has the correct geometry for adsorption on a calcite surface, where each PO_3 unit coincides with a CO_3 unit in an adjacent layer; this prevents adsorption of a further calcium ion layer and hence prevents crystal growth.[76,77,194] As a consequence, calcium carbonate in particular is retained in solution in an apparently supersaturated or other metastable condition[142,166] rather than as a stable true complex.[169] Other possibilities such as the reduction of calcium activity by an unspecified mechanism, colloid formation,[148] prevention of calcium carbonate formation from calcium bicarbonate and prevention of nucleation, have been rejected in the light of later work.[142,165,319,326,327] If precipitation is retarded, the effect is said to be fairly permanent; the threshold concentration is increased by adding ammonia or by increasing the concentration of calcium bicarbonate, but ammonium salts and simple sodium salts increase the effectiveness of the polyphosphate: these effects may well be explained by the effect of the added salts on the activity of calcium ions.[327] When delayed precipitation does occur, for example after an increase in temperature of the solution, fewer crystals of a grossly distorted nature are formed, compared with normal products when polymetaphosphate is absent; this observation has been made also with other phosphates but to a less degree. In the distorted crystals, only one atom of phosphorus is found for every three hundred of calcium, but the calcite lattice does not appear to be distorted.[322,326] When magnesium is also present in the solution, however, it appears in the delayed precipitate, and in this case the lattice is distorted.[322] By choice of seeding and other conditions it is possible to precipitate calcite, vaterite, aragonite or a calcium carbonate monohydrate.[322]

Sequestration appears to depend upon ion association, rather than on true complex formation; claims for the formation of complexes of the type

$Na_4[Ca(PO_3)_6]$ were taken to confirm the hexameric formula for Graham's salt, but it has been shown that only one calcium, magnesium or zinc ion is associated with at least 5 or 6 monomeric metaphosphate units in the chain.[22] The supposition of ion association is in accord with the observation that variation of hydrogen ion concentration (provided that it does not exceed 10^{-5}N.) has little effect.[22] Owing to sequestration, probably of the ion association type, ferric ions are not strongly retained on a cation exchange column when glassy sodium polymetaphosphate is present in the solution.[325] Association of sodium ions in solutions of the glassy metaphosphate increases with increasing chain length, and when strontium ions replace those of sodium at any given chain length the mobility and charge of the anion are not affected.[275]

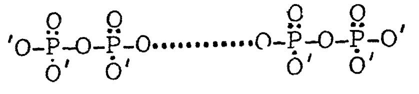
The low concentrations of Graham's salt used for scale prevention have also a value in inhibiting the corrosion[77,165,171,193,194] of aluminium, iron, copper, iron oxide, copper oxide and other surfaces. The mechanism suggested is the formation of a barrier of adsorbed polymetaphosphate[165,171,193,194] or other adsorption layers[328] such as a mixture of corrosion products with polymetaphosphate,[205] or calcium carbonate stabilized against growth by adsorbed metaphosphate ions.[76,77] On the other hand, lead[329] and magnesium,[330] the ions of which are sequestered by the salt, are rapidly corroded. Potentials of iron cathodes in experimental aeration cells containing a solution of glassy sodium polymetaphosphate are decreased while those of the anodes are increased: this causes a decrease in potential difference and hence a drop in the corrosion current.[328] When calcium sulphate and the polymetaphosphate are present together in an electrolyte in contact with a zinc and an iron electrode, the current decreases to a steady minimum within 17 hours owing to barrier formation on the iron cathode only; it is essential that carbon dioxide be present in this experiment, presumably to allow calcite formation.[77] A similar experiment with a copper–iron electrode system showed that Graham's salt alone was sufficient to reduce the anodic nature of the iron and at the same time increase cathode polarization.[204,206,331] The barrier causes polarization, which reduces corrosion, and also provides a high-resistance layer which reduces the corrosion current.[328,331] The corrosion current, I, expressed in terms of open circuit potential, E_0, (approximately the reversible potential), electrode potentials, E_a and E_c, and electrolyte resistance, R_e, has been measured: the marked reduction in E_0 (see Table XXXVIII) is said to account for the inhibitory action of the polymetaphosphate introduced into the electrolyte.[207]

TABLE XXXVIII. - ELECTRICAL DATA FOR THE INHIBITORY ACTION OF GLASSY SODIUM POLYMETAPHOSPHATE

No inhibitor		50 p.p.m. of 'Calgon' present	
At 24 hr.	At 120 hr.	At 24 hr.	At 120 hr.
I 0·50ma.	0·52ma.	0·08ma.	0·01ma.
E_0 0·08V.	0·08V.	0·08V.	0·02V.
E_a 0·06V.	0·05V.	0·01V.	0·005V.
E_c 0·02V.	0·03V.	0·07V.	0·015V.
R_e nil	nil	nil	nil

Neglecting minor variations due to different details of the method of preparation of Graham's salt,[5,27,122] molecular size determinations fall into two main groups. For the number of monomeric metaphosphate units per anion, low figures of 4 (cryoscopy[266]), 8 (viscometry of melt[261]), 9 (surface tension of melt[258]) and up to 9 (X-radiography[66]) have been taken to support a random reorganization theory[258] of the condensed anion in the melt, and the cryoscopic values have been rejected.[22] High figures of 70 to 190 (viscometry and light-scattering in aqueous solutions[267,269]), 108 to 172 (anion-exchange and end-group titration[305,312]), 150 (transport measurements[275]), 255 (flow birefringence[273]), 1400 (dispersion measurements[271]), 100 to 13,000 (sedimentation equilibria[5,272]) and 'high' (of colloidal dimensions),[6] are taken to support the linear high-polymeric anion theory of solution and solid. It is generally agreed that 'sodium hexametaphosphate' is not a true hexamer,[5,6,22,27,68,325,332] and even if cyclic[66,273] and branched[267,269] structures are present in the linear polymer[254,273] they contribute but little to the mainly rod-like polyanion,[55,254] and internal rotation is sterically almost unhindered.[269] The similarity to, but not identity with, Kurrol fibrous sodium polymetaphosphate has been pointed out.[55,333,334]

It is said that at infinite dilution the anion is rod-like and only curls or spirals in appreciable concentrations or in the presence of simple electrolytes.[55,267,269] It has been suggested that the polyanion has a structure that can be formally written:-[92,312]



$$'\text{O}-\underset{\text{O}'}{\overset{\text{O}}{\text{P}}}-\text{O}-\underset{\text{O}'}{\overset{\text{O}}{\text{P}}}-\text{O}\cdots\cdots\cdots\cdots\text{O}-\underset{\text{O}'}{\overset{\text{O}}{\text{P}}}-\text{O}-\underset{\text{O}'}{\overset{\text{O}}{\text{P}}}-\text{O}'$$

in which the tetrahedral PO_4 units recur regularly so that only the end-groups are of distinctly different dissociation constant from the remainder; this particularly applies to the parent acid.[276] Although it might be expected that the degree and type of polymerization would differ as between solution and solid, X-radiography shows no difference between the two states.[66] It is now generally agreed that the average chain length in any given preparation is approximately 100 to 200 monomeric units,[21] and that the very large values obtained in the ultracentrifuge may be due to micellar aggregation of these polymers; micellar aggregation of smaller units[68] to give apparent molecular weights of approximately 10,000 to 20,000 does not appear to be a sound theory in the light of conductivity measurements.[6] Molecular weights of glassy sodium polymetaphosphates are smaller than those of analogous potassium compounds.[272] The similarity between the geometry of the structures of the repeating -P-O-P-O groups, not found in the cyclic metaphosphates, and that of the calcite lattice has been pointed out.[76,77]

In simple mixtures, sodium metaphosphate glass is determined as orthophosphate by standard methods after hydrolysis with dilute nitric acid.[41,44,289,335] In a mixture of sodium phosphates, the linear polymetaphosphate is quantitatively precipitated with barium chloride solution, leaving all other phosphates in solution; the precipitate is unsuitable for weighing, but can be hydrolyzed with nitric acid and determined as orthophosphate with magnesia mixture.[41] The precipitates formed with barium chloride[41] and with silver nitrate[6,336] form delicate tests for the salt when interfering substances are absent.

3. 'Insoluble' Sodium Metaphosphate, $NaPO_3$-IV, (Kurrol salt).

The first recorded recognition of a further 'insoluble' form of sodium metaphosphate was made in 1890.[337,338] The method of preparation by controlled cooling and seeding of sodium metaphosphate melts[337] has been confirmed[47,48,54,55,78,79,108,339] but the method of slow dehydration of sodium dihydrogen orthophosphate[338] has not. Sodium dihydrogen orthophosphate, disodium dihydrogen diphosphate or a mixture of sodium dihydrogen orthophosphate (85 parts) and ammonium dihydrogen orthophosphate (15 parts) or any sodium metaphosphate is heated to at least the melting point of the metaphosphate that is formed: the melt is cooled over 2 hours to 580°–590°C. and is then 'seeded' either with previously prepared Kurrol salt or with carborundum or silica or sodium metaphosphate type II and the temperature is held at 560° to 570°C. for 70 to 90 minutes. After chilling, the upper layer of trimetaphosphate is broken away to leave a 90 to 95% yield of the Kurrol salt.[55] Traces of the salt are often observed during the cooling of molten metaphosphate, but this appearance is capricious. It has been noted that good yields are more likely to result when the sodium to phosphorus ratio is greater or less than exactly 1 to 1:[22,55,339] this may hinder the development of sodium trimetaphosphate, but the sodium to phosphorus ratio in the fibres obtained in such cases has not been reported. It has been said that the type-IV metaphosphate is also produced from sodium trimetaphosphate *via* an intermediary tetrametaphosphate[78,79] and by heating sodium alkyl hydrogen orthophosphates to incipient red-heat,[48] but this has been confirmed only for the analogous potassium salts.[15] Nevertheless, the product can be used satisfactorily for 'seeding' the metaphosphate melt during the production of genuine Kurrol salt.[48]

No widespread use of Kurrol salt has been recorded, but patents refer to its application in the treatment of hard waters, which it softens efficiently in the presence of potassium sulphate as stabilizing agent,[108] and in the thickening and stabilizing of milk-protein products.[340]

Sodium polymetaphosphate type IV exists in two crystalline forms: type A, density 2·851 (2·581?), which is converted to type B under pressure or by moisture, this form being needle-like with a density of 2·558 at 20°C.[55] A preparation described as 'feathery' has *d* 2·56 (large pieces) or 2·62 (small pieces).[339] The crystals resemble asbestos and are difficult to grind.[1] *X*-Ray investigation shows remarkable similarity between different preparations.[22] Diffraction patterns have been published and compared with those of other sodium metaphosphates.[1] Crystallographic data are given in Table XXXIX.

TABLE XXXIX. - CRYSTALLOGRAPHIC DATA FOR KURROL SALTS[341,342]

Property	Fibrous[341]	$NaPO_3$-IVα (IVA?)[342]	$NaPO_3$-IVβ (IVB?)[342]
a_1 (A.)	23·76	-	-
a_2 (A.)	6·09	-	-
a_3 (A.)	14·07	-	-
a (A.)	-	12·12	11·37
b (A.)	-	6·20	6·02
c (A.)	-	6·99	7·64
β(°)	90·8	88	86
Mol./unit cell	32	8	8
Space group	$B2_1/c$	$P2_1/n$	$P2_1/n$
Density (g./c.c.) (obs.)	-	2·54–2·60	2·54–2·60
Density (g./c.c.) (calc.)	-	2·58	2·60

The unit cell is monoclinic and crystals twinned on the (100) plane are pseudo-rhombic.[341] Infra-red absorption data are presented in Table XXXVI.[70] The melting point is 628°C.[22,54,55] A melting point of 809° to 811°C. has been given for a variety which is unchanged on melting,[48] but this has not been substantiated.[53] The salt is slowly soluble in cold water to give solutions up to at least 1% in strength.[21,22] The dissolution proceeds by process of swelling and gel-formation and results in a viscous solution comparable with glycerol. Warm water increases the rate of dissolution but also causes chemical breakdown which results in reduced viscosity. Addition of salts other than those of sodium (e.g., ammonium chloride,[112] potassium sulphate,[108] lithium chloride,[339] ammonium salts, amines and potassium polymetaphosphate[22]) greatly accelerates the swelling and dissolution process with accompanying reduction in viscosity. The effect of the salts is in the order: K>Li>NH_4>Rb>amines, the last being only weakly active.[22] The salt can be recovered from these mixed solutions by addition of large quantities of ammonium, sodium or potassium chlorides[339] or of ethanol.[112,339] The product so precipitated is more soluble in water than the starting material, and it seems probable that some depolymerization has taken place.[112] An insoluble polymetaphosphate ($NaPO_3$-IV?) is soluble in sodium pyrophosphate solutions and the polymetaphosphate can be recovered by adding concentrated sodium salts or a little acetic acid: evaporating the coagulum to dryness in a vacuum gives a rubber-like mass which is soluble in water giving viscous solutions.[343] On the other hand, Kurrol salt is said to be insoluble in sodium meta- and pyro-phosphate solutions.[339] Viscosity measurements have been made on aqueous solutions of the salt,[112,343] and its dispersing action on solid particles has been noted.[340]

On heating to fusion, Kurrol salt forms a typical sodium polymetaphosphate melt at 628°C., irrespective of the rate of heating. From the melt other sodium metaphosphates can be obtained: Graham's salt by rapid chilling, trimetaphosphate by tempering, etc. The processes seem to be autocatalytic.[48] The trimer can also be obtained by tempering the salt, especially type B,[55] at 380° to 625°C. (*i.e.*, below the fusion point)[21,22,37] and insoluble sodium metaphosphates, type II and possibly -III, can be prepared from type A[55] at 380° to 390°C.

Hydrolysis of all forms of Kurrol salt leads ultimately to the sodium orthophosphate series. In acid solutions pyrophosphate, but not trimetaphosphate, appears to be an intermediate.[55] Similar products are obtained in neutral solution (the isolation of 50% of orthophosphate with 2 to 5% of pyrophosphate has been quoted) but sodium trimetaphosphate has also been isolated (48 to 45% in the example given, after 7 hours at 70°C.) in a reaction analogous to the hydrolysis of glassy sodium polymetaphosphates and insoluble sodium metaphosphate-II.[55,61] The trimer is not a direct hydrolysis product, but is formed in a secondary cyclization process.[55]

The salt forms complexes with calcium and magnesium,[108] and with iron and uranium[46] analogous to those of Graham's salt but their stability is said to be greater, especially in boiling solutions.[108] The complex formation appears to take place by a mechanism of ion association or ion exchange.[339]

It is agreed that the salt is the sodium compound of a long-chain polymetaphosphate anion[22,55,112,339,341,343] which resembles but is not identical with that of glassy sodium polymetaphosphate.[333,334] Estimates of 10,000 (viscometry[112]), 14,000 (viscometry[339]) and[21] 500 to 1000 monomeric metaphosphate units per chain have been made. The monomer units are those of PO_3 tetrahedra repeating themselves in the chain at every fourth with an interval of 6·02A.[21] in a formation similar to that of the enstatite SiO_4 chain.[341] The end-groups are relatively strongly dissociated.[55] That the repeating -P-O-P-O units are of the proper geometric spacing to be adsorbed on the calcium carbonate lattice accounts for the ability of Kurrol salt to prevent scale formation and to soften water.[22,76]

Other Sodium Metaphosphates.

Whereas it is now recognized that commercial or undried melts of sodium metaphosphate that have been chilled contain mainly vitreous sodium polymetaphosphate, they also contain appreciable quantities of acid triphosphates. These do much to enhance the water-softening properties of the product. Several other 'metaphosphates' have been prepared, usually commercially; these are claimed to be sodium metaphosphate but are actually sodium polymetaphosphate glass with greater proportions of various sodium polyphosphates.[344] They have industrial application in water treatment, in which they are quite efficient because of their constituents, and are prepared by heating a suitable sodium salt with phosphoric acid at >300°C.[345] or a sodium metaphosphate with phosphorus pentoxide.[346,347] Extensive physicochemical investigations have been made on the series of sodium phosphate glasses in the range of compositions between Na_2O to P_2O_5 ratios of 1:1 to 2:1.[270,348]

Various isolated and unsubstantiated references have been made to other sodium metaphosphates:- (*a*) an acid polymetaphosphate, $[Na_2H(PO_3)_3]_n$, *i.e.*, an acid polytrimetaphosphate, is obtained on heating sodium dihydrogen orthophosphate with phosphoric acid at >300°C.; the product has a definite *X*-ray diffraction pattern and a melting point of approximately 420°C.; it is probably a long-chain polymetaphosphate.[96] (*b*) If phosphoric acid is heated at 300°C. in a gold boat under vacuum for a few hours an acid is produced with the empirical formula of metaphosphoric acid; the sodium salt of this acid is prepared in solution at 0°C. by adding a sodium base and the salt is precipitated with ethanol as an oil which does not crystallize and has no definite *X*-ray diffraction pattern. By cryoscopy at the potassium nitrate-water eutectic, analogous potassium salts have been shown to have twelve monomeric metaphosphate units per anion.[349] (*c*) A sodium metaphosphate hemihydrate of unspecified polymeric condition is formed on heating disodium ammonium hydrogen diphosphate at 320°C.[106] (*d*) There is some evidence from paper-chromatography for the presence of 3, 4 and possibly 5 to 8- or more membered ring sodium metaphosphates in the solutions obtained after partial hydrolysis of Graham's salt.[310,311]

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SECTION XXXIX

THE SPECTROSCOPY OF SODIUM AND CERTAIN OF ITS COMPOUNDS

By R. F. BARROW and LADY ANNE THORNE

THE SPECTRUM OF ATOMIC SODIUM

By A. THORNE

Introduction

The spectrum of atomic sodium has been much investigated since the early days of spectroscopy, and indeed the study of the alkali metal spectra played an important part in the development of modern spectroscopic theory. Brief historical accounts are given in many of the standard text-books[1-3] and in review articles.[16,17]

A description of the sodium spectrum and its explanation in terms of modern theory is to be found in these and other text-books.[1-6] The neutral sodium atom has the ground state electron configuration $1s^2\ 2s^2\ 2p^6\ 3s\ ^2S_{1/2}$, with the $3s$ electron outside a neon-like core of closed shells. This gives rise to a doublet spectrum in which the resonance doublet, $3p\ ^2P_{3/2,1/2} - 3s\ ^2S_{1/2}$, constitutes the well-known yellow *D*-lines at 5896 A. and 5890 A. The rest of the principal series is in the ultra-violet region. The sharp and diffuse series lie mainly in the visible region, and the fundamental in the infra-red.

The most important energy levels and transitions in the spectrum of Na I are shown diagrammatically by Grotian.[7] Numerical values of the energy levels of Na I, II, and III have been tabulated by Bacher and Goudsmit,[8] and in 1949 the National Bureau of Standards published more comprehensive tables of energy levels for spectra up to Na IX.[9]

The wave-lengths of observed lines of Na I were first listed in their series by Fowler[10] and Paschen-Götze.[11] Later tables compiled by Moore[12,13] give many multiplets of Na I and II and a few forbidden lines of Na IV and V from 13,000 A. to the vacuum ultra-violet, together with a finding list arranged by wave-length. The M.I.T. wave-length tables[14] list the arc and spark lines of all elements between 10,000 A. and 2,000 A. and include a list of the 'raies ultimes'; these are also given in the Vatican Observatory 'Atlas of Persistent Spectra'.[15]

In 1938 Shenstone[16] published a review with tables showing the completeness with which the arc and various spark spectra of every element had been investigated at that time, and in 1946 Meggers[17] brought the information up to date. At the same time Hartree presented in a similar way a summary of the calculations of atomic structures.[18] Both theoretically and experimentally, the spectrum of sodium is one of the best known of all.

In astrophysics, lines of the sodium spectrum are of such importance that a separate sub-section is devoted to the subject (see page 1367).

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Excitation

The spectrum of sodium has been excited in flames, arcs, sparks, and various forms of discharge and also observed by several methods in absorption. In this sub-section reference is made only to those papers in which the conditions or mechanism of excitation has been the main consideration. Wavelength and intensity measurements of spectral lines and accounts of specialized sources for particular investigations are described in other sub-sections; in particular, references to various forms of spark source are given in the sub-section on ionized sodium (see page 1357).

Flames, Furnaces and Collision Processes.

Many investigations have been made of the relation between the intensity of the spectral lines absorbed and emitted by sodium atoms in various sorts of flame and the concentration of the sodium salts.[1-9,100] This relation has generally been found to follow a linear law at low concentrations and a square root law at higher concentrations. Various methods of introducing the salt into the flame have been described.[1,3,9,91] The distribution in the flame of the excited atoms and the mechanism of excitation,[3-6,10,11,100,101] the effects of adding salts of other alkalies,[12,13] and photoluminescence in flames[14] have all been studied in some detail.

Both emission and absorption spectra have been examined in the electric furnace and in exploding wires.[15,16]

The 'reversal temperature' of the *D*-lines (*i.e.*, the brightness temperature of a continuous background against which they just vanish) has been used to measure flame temperatures,[17-19,99] and the advantages and limitations of the method have been discussed.[20] It has recently been applied to research in combustion[92-94] and to the detection of atmospheric particles containing sodium.[95]

Chemiluminescence effects arising from interactions of sodium vapour with atomic hydrogen[21,22] and with the halogens[23-26] have been investigated. Excitation of the sodium spectrum by active nitrogen has been attributed to both chemiluminescence and collision processes,[27-30,96] and attempts have been made to determine the form of collision process responsible for excitation by mercury[31,32] and hydrogen atoms[33-35,90] and by helium.[90]

Arcs.

There have been many investigations of the influence of arc current and voltage on the number and intensity of the sodium lines excited and on the spatial distribution of excited atoms and ions in the arc.[36-46] Enhanced lines have been produced by interrupting the arc,[47,48] and the properties of vacuum arcs have been studied.[49-51] In view of the importance of arc sources in spectrochemical analysis, the relative intensities and reproducibility of the lines are of particular interest.[52-57] Small quantities of sodium are found to affect the excitation of the spectra of other metals.[97]

Discharges.

Glow discharges in sodium vapour were early investigated both for their possibilities as commercial lamps and for their physical interest.[58-62] The mechanism of both the positive column[63-67] and the cathode glow[68-70] have been studied; the latter, in the form of the Schüler hollow cathode discharge, has been used to excite spark spectra and is of particular importance in high resolution work. From the positive column have developed commercial sodium lamps, usually run in argon or neon and sometimes using a mercury–sodium amalgam.[71-78,98]

The ionization potential of sodium and the excitation potentials of the different energy levels have been measured by exciting discharges with electrons of known voltage and plotting line intensity as a function of electron voltage.[79-85] In some cases excitation cross sections have also been estimated. The existence of Na^- ions has been shown by mass spectroscopy, the ratio $Na^-:Na^+$ being about $1:10^4$.[86]

The electrodeless discharge in sodium was discovered early[86,87] and was later applied to excite atomic beams.[88] Like the hollow cathode discharge it has found important applications in high resolution spectroscopy and the excitation of spark spectra.

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The Spectrum of Neutral Sodium

The neutral sodium atom has the ground state configuration $1s^2\ 2s^2\ 2p^6\ 3s\ ^2S_{1/2}$, with an ionization potential of 5·138 V., corresponding to a term value for the ground state of 41,449·65 cm.$^{-1}$, or a wave-length limit of 2411·83 A. for the principal series.[1] The most recent value for the ground term is actually a little lower, namely, 41,449·44 cm.$^{-1}$.[6]

The results of early work[7-10] are summarised in Fowler's tables,[4] which include the first 55 members of the principal series. Certain additions and corrections were made in later investigations,[11-13] among them some very accurate interferometric measurements on the lower members of the principal, sharp and diffuse series.[14-16] A number of these and a few forbidden lines are listed and classified in Moore's multiplet tables.[2,3] Experimentally determined energy levels are listed in the National Bureau of Standards 'Atomic Energy Levels',[1] published in 1949. Term values are given for all excited states of the $3s$ electron up to $14s$, $59p$, $15d$ and $11f$ respectively, based on the papers referred to above but modified where necessary to include the 1949 results of Thackeray.[5] Actually Thackeray's measurements on the principal series in absorption extended as far as $n = 73$, and he also measured the $3s - nd$ series as far as $n = 13$; his paper includes a critically compiled table of energy levels, in which his own results are supplemented by those of earlier workers.

In 1956 another set of measurements was made on the Na I spectrum, this time in emission, by Risberg.[6] Combining his results on 45 lines with the earlier interferometric measurements of Meissner and Luft,[16,17] Risberg constructed a new table of energy levels for states up to $12s$, $8p$, $6d$ and $10f$ respectively, differing slightly from those given by Thackeray. The extended Ritz formulæ calculated by Risberg[6] reproduce the observed energy levels well in all four series, but particularly in the sharp and fundamental series. He therefore used these two to determine the series limit, for which his value of 41,449·44 ± 0·02 cm.$^{-1}$ differs from Thackeray's[5] value of 41,449·65 ± 0·02 cm.$^{-1}$ derived from an extrapolation of measurements on the principal series. Risberg, examining the discrepancies between his calculated and Thackeray's measured value for the principal series, concludes that Thackeray may have underestimated his errors and that his results for the higher series members may have been affected by pressure shifts.

The doublets of the principal series have been resolved as far as $n = 9$ by Thackeray,[5] using a grating spectrograph. The 3 ^2P and 3,4,5,6 ^2D doublet

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splittings are known very accurately from the interferometric measurements of Meissner and Luft.[16,17] The splittings are given in Table I, where the minus sign for the ^{2}D doublets indicates that they are inverted. The reason for this inversion is discussed later (see page 1364).

TABLE I. - DOUBLET INTERVALS IN THE SPECTRUM OF Na I.

n	3	4	5	6	7	8	9
$\Delta\nu$ (*np* ^{2}P) cm.$^{-1}$	17·1963	5·63	2·52	1·25	0·74	0·47	0·47
$\Delta\nu$ (*nd* ^{2}D) cm.$^{-1}$	-0·0494	-0·0346	-0·0230	-0·0124	-0·001	-	-

Forbidden lines of the 3*s* - *nd* series have been found in both absorption and emission.[5,6,20-23] Their transition probabilities have been measured by the method of anomalous dispersion[22,23] and shown to agree with those to be expected from quadrupole radiation.[23,24] Measurements have also been made on the 3*p* - *np* series,[25-27] for which intensities have been calculated by a perturbation method.[28] The appearance of forbidden lines of both the *s* - *d* and *s* - *s* series in strong electric fields is discussed later (see page 1360). Two review articles on forbidden lines contain references to sodium.[18,19]

Continuous emission spectra have been observed in sodium, corresponding to recombination of an electron and an ion to form a neutral atom either in the ground state or in the first ^{2}P state.[25,27,38] The continuous absorption (photoionization) spectrum has been much investigated.[29-36] Ditchburn *et al.*[36] have summarized continuous absorption results for all the alkali metals; the curve of atomic absorption coefficient against frequency shows a characteristic minimum, which for sodium lies at about 1900 A., and there appears to be a discontinuity at or very near the series limit. The behaviour of the curve is in qualitative agreement with the calculations of Seaton.[37] Calculations of continuous absorption coefficients are also mentioned elsewhere (see page 1364).

Calculations of line transition probabilities are also discussed later (see page 1364). As regards their experimental determination, full general accounts have been given by Mitchell and Zemansky,[39] with many references to work on sodium, and more recently by Unsöld.[40] The transition probabilities of the yellow *D*-lines have been particularly thoroughly investigated. Apart from direct lifetime measurements,[41,42] their *f*-values have been estimated from their absolute emission[43-45,47] and total absorption[48] intensities and from line emission and line profile measurements.[49-52] The *f*-values have also been found from measurements of the anomalous dispersion[56,57,59,60] (including the Roschdestwenski 'hook' method)[61] and magneto-rotation.[52,56] Measurements by the null method of magneto-rotation[53-55] do not require an independent determination of the vapour pressure; the most recent measurement was made by this method[55] and yielded *f*-values of 0·325 and 0·650 for the 3 $^2S_{1/2}$ - 3 $^2P_{1/2}$ and 3 $^2S_{1/2}$ - 3 $^2P_{3/2}$ lines respectively, corresponding to a lifetime of 1·61 ± 0·06 × 10^{-8} sec. for the 3 ^{2}P state.

f-Values for the higher members of the principal series have been found relative to those for the *D*-lines by emission,[66,67] absorption,[65] and anomalous dispersion[58] measurements. In the sharp and diffuse series the absolute emission[46,68] and 'hook'[62,63] methods have been applied and, more recently, a method based on the Stark effect splitting.[64]

The subject of the doublet intensity ratio has attracted much attention in all alkali metal spectra. The ratio has been measured in the sodium *D*-lines by all the methods mentioned above;[44,49,50,55,69-77] except in special conditions[72,76,77] the value, within experimental error, is found to be the theoretical one of 2:1, and the same has been found for doublets of the sharp and diffuse series.[70] Theoretical reasons for the departure from the 2:1 rule, slight in sodium but much more notable in the heavier alkalies, have been discussed.[78-80]

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The Spectrum of Ionized Sodium

Singly Ionized.

Lines of the Na II spectrum were early observed in several different kinds of source: discharge tubes,[5,10] electrodeless discharges,[6] and interrupted arcs;[7,8] and their conditions of excitation were studied in various forms of spark and condensed discharge.[9-14] Hollow-cathode discharge tubes[15,21] and electrodeless discharges[16,27] have been used as well as sparks in systematic investigations of the spectrum. The lines excited have been listed and classified in a number of papers,[15-23] notably one by Söderquist,[4] who, from his and earlier results, compiled a complete set of tables of wave-lengths and energy levels. The measured wave-lengths, classifications, and intensities of many of these lines are given in Moore's multiplet tables.[2,3]

Na II has a neon-like spectrum with the ground state electron configuration $1s^2\ 2s^2\ 2p^6\ {}^1S_0$. The ionization potential is 47·29 V., corresponding to a ground term value of 381,528·cm.$^{-1}$ relative to the $^2P_{3/2}$ ground term of Na III; referred to the $^2P_{1/2}$ term of Na III the value is 382,892 cm.$^{-1}$.[1,4] The 23 terms listed in the National Bureau of Standards 'Atomic Energy Levels'[1] are based on Söderquist's paper.[4] They arise from the configurations $2p^5$ 3,4,5,6 s; $2p^5\ 3p$; $2p^5$ 3,4 d; and are built on both the $2p^5\ {}^2P_{3/2}$ and $2p^5\ {}^2P_{1/2}$ terms of the ion.

Doubly Ionized.

Na III has a fluorine-like spectrum with an ionization potential of 71·65 V., corresponding to a term value 578,033 cm.$^{-1}$ of the $1s^2\ 2s^2\ 2p^5\ {}^2P_{3/2}$ ground state.[1] Söderquist's comprehensive paper[4] lists the lines measured by himself and earlier workers[23-25] and the energy levels derived therefrom. These, with later additions by Tomboulian,[27] form the basis of the 34 terms listed in 'Atomic Energy Levels', arising from the configurations $2s\ 2p^6$; $2s^2\ 2p^4$ 3,4s; $2s^2\ 2p^4\ 3p$; $2s^2\ 2p^4$ 3,4d.

More Highly Ionized.

The spectra of the ions Na IV to Na IX lie in the vacuum ultra-violet region and have all been investigated by Söderquist, using a vacuum spark and

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grating spectrographs with which he was able to photograph lines down to the wave-length 50 A. His 1934 paper[4] gives his first results for all these spectra (including his own and other earlier work on Na IV);[23,26] to these he added additional measurements and classifications in 1946 for Na IV, V and VI[28] and in 1944 for Na VII, VIII and IX.[29] His term values and ionization potentials are quoted in 'Atomic Energy Levels'.[1] Table II indicates the extent of the data given on each spectrum. The starred values for the ionization potentials of Na X and XI are taken from a recent paper by Finkelnburg,[30] who obtained them by extrapolating both along iso-electronic sequences and up the appropriate columns of the periodic table.

Forbidden transitions in the spectra of Na IV, V and VI have been further discussed with reference to their astrophysical importance.[31]

TABLE II. - DATA FOR THE SPECTRA OF THE IONS Na IV TO Na XI.

Spectrum	Iso-electronic with	Ionization potl. volts	Series limit cm.$^{-1}$	Ground State	No. of class. lines	Wave-length region A.	No.of terms given
IV	O I	98·88	797,741	$1s^2\ 2s^2\ 2p^4\ {}^3P_2$	74	129-412	40
V	N I	138·60	1,118,170	$1s^2\ 2s^2\ 2p^3\ {}^4S_{3/2}$	203	100-514	45
VI	C I	172·36	1,390,558	$1s^2\ 2s^2\ 2p^2\ {}^3P_0$	134	80-638	63
VII	B I	208·444	1,681,679	$1s^2\ 2s^2\ 2p\ {}^2P_{1/2}$	158	62-491	68
VIII	Be I	264·155	2,131,139	$1s^2\ 2s^2\ {}^1S_0$	86	51-117	27
IX	Li I	299·78	2,418,520	$1s^2\ 2s\ {}^2S_{1/2}$	22	44-81	15
X	He I	1465·*					
XI	H	1646·*					

*Values by extrapolation.[30]

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Zeeman and Stark Effects

Zeeman Effect.

The Zeeman effect in the alkali metal doublets is described in text-books on spectroscopy, for example those cited in the Introduction. Rather fuller accounts have been given by Back and Landé,[1,2] and magneto-optical phenomena arising from the Zeeman effect are described by Wood[3] with particular reference to sodium. As the historical resumés in these books indicate, the 'anomalous' Zeeman pattern of the *D*-lines played an important part in the development of spectroscopic theory.

The Landé *g*-factor for the $^2S_{1/2}$ ground state of sodium is 2, and for the $^2P_{1/2}$, $^2P_{3/2}$ levels it is 2/3, 4/3 respectively. In a magnetic field not strong enough to break down the spin-orbit coupling, the Zeeman pattern, in terms of the classical Lorentz splitting $\Delta\nu_L$, consists for the $^2S_{1/2} - {}^2P_{1/2}$ line of two π-components at $\pm\frac{2}{3}\Delta\nu_L$ and two σ-components at $\pm\frac{4}{3}\Delta\nu_L$, and for the $^2S_{1/2} - {}^2P_{3/2}$ line of two π-components at $\pm\frac{1}{3}\Delta\nu_L$ and four σ-components at $\pm\frac{2}{3}\Delta\nu_L$, $\pm\frac{5}{3}\Delta\nu_L$. As the magnetic field becomes strong enough to break down the spin-orbit coupling, the components of both lines merge and tend towards the Paschen-Back pattern, consisting solely of a π-component in the position of the field-free line and σ-components at $\pm\Delta\nu_L$. The Zeeman effect in the alkali metals has been treated mathematically on the basis of Dirac's theory.[4]

The magnetic double refraction of sodium vapour has been measured and compared with the calculated effect.[5] It has been shown from the Zeeman effect of the 'forbidden' $3s - nd$ lines that they should be ascribed to quadrupole radiation.[6,7] The effect of high pressures on the Zeeman pattern of the *D*-lines[9,37] and the appearance of forbidden components in it[8,9] have been described and the intensity to be expected in these components has been calculated.[35,36]

The Zeeman effect in the ground state of sodium has received much attention in atomic beam magnetic resonance experiments (see page 1362), in the course of which extremely accurate measurements of the Zeeman splitting have been made. The $g(^2S_{1/2})$ values for lithium, sodium and potassium are found to agree to 1:40,000,[41] and the $g(^2S_{1/2})$ value of sodium has been compared with that of other atoms as part of a precision determination of the value g_S of the electron.[40-42] Reasons for small discrepancies have been suggested.[43]

The simple Zeeman pattern in any field is symmetric about the field-free line. However, at high fields and for the higher members of a series, the pattern as a whole may be asymmetrically shifted by the so-called quadratic effect. A brief account of this has been given by White[10] with references to the work done on sodium.[11,12] The centre of gravity of the σ-components should be shifted twice as far as that of the π-components, the shift being proportional to H^2 and to $(n^*)^4$ where n^* is the effective quantum number. The experiments of Jenkins and Segré[12] in the principal series of sodium have confirmed these relations as far as $n = 20$; extra displacements with considerable broadening from $n = 20$ to $n = 35$ were ascribed to perturbation of the ^2P levels by neighbouring ^2F levels.[12,13]

Stark Effect.

The Stark effect is rather briefly discussed in most text-books. A fuller account has been given by Minkowski,[14] and electro-optical phenomena in

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sodium vapour are also discussed by Wood.[3] The Stark pattern is considerably more complicated than the Zeeman pattern. In the alkali metals the first-order effect is a quadratic one: an asymmetric splitting proportional to the square of the field strength. When unresolved this appears as a simultaneous broadening and shift of the line. The theory has been discussed in several papers.[15-17,38] The quadratic effect has been observed in emission in sodium by various methods for members of the principal, sharp and diffuse series.[18-22,39] The effect appears to increase less rapidly with increasing principal quantum number than is predicted by theory.[20,21] The quadratic effect has also been studied in absorption (inverse Stark effect) in the principal series,[20-28] and the shifts found to vary, as they should, with the square of the field strength.[24,27,28,31] In absorption measurements, the electric field is found to influence the intensities of the $3s - nd$ and $3s - ns$ forbidden series,[30,31] an effect which has also been discussed theoretically.[32] Electric double refraction in sodium vapour in the neighbourhood of the D-lines has been studied and found to be anomalous owing to a larger shift for the π-component than for the σ-component in the D_2-line.[25,26,28-30]

Magnetic and electric fields have been combined to observe their effect on the higher members of the principal series in absorption[33] and the depolarization of the Zeeman components.[34]

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Hyperfine Structure and Nuclear Moments

Before the development of magnetic resonance techniques nuclear moments were determined primarily by optical investigation of the hyperfine structure (hereafter referred to as hfs). The theory is given in Kopfermann's book,[1] which also describes the methods used in both optical and radiofrequency spectroscopy. The methods of obtaining nuclear moments are also summarized by Ramsey,[2] with tables of results up to 1952 and many references. Nuclear effects in atomic spectra[47] and the rôle of nuclear moments in the shell model of the nucleus[49] have recently been reviewed. The data for the sodium isotopes, with references, are summarized in Table III. The columns headed $\Delta\nu(3^2S_{1/2})$ refer to the splitting between the two hyperfine levels of the $3^2S_{1/2}$ ground state; this has been measured much more accurately by radiofrequency methods than is possible optically (as has the magnetic moment),[48] but the first few figures of the value converted to cm.$^{-1}$ have been given here for convenience. *I* is the nuclear spin, μ the nuclear magnetic moment (in nuclear magnetons) and *Q* the nuclear electric quadrupole moment.

TABLE III. - NUCLEAR MOMENTS OF THE SODIUM ISOTOPES

	I	μ (n. m.)	$Q(\times 10^{-24}$ cm.$^2)$	$\Delta\nu(3^2S_{1/2})$ mc/s	$\Delta\nu(3^2S_{1/2})$ cm.$^{-1}$
^{22}Na	3[2]	+1·74582[2] ±0·00030	-	1220·64[2] ± 0·04	0·0407
^{23}Na	3/2[2]	+2·21714[31] ±0·00012	+0·10[33,34,35] ±0·01	1771·61[2] ± 0·03	0·0591
^{24}Na	4[27]	+1·688[27] ±0·005	-	1139·35[27] ± 0·10	0·0380

In optical spectroscopy attention has been mainly focused on the hyperfine structure (hfs) of the *D*-lines of ^{23}Na, the only stable isotope. The structure is due mainly to the splitting of the $3^2S_{1/2}$ ground state, that of the $3^2P_{1/2}$ state being about one-tenth of the former, and that of the $3^2P_{3/2}$ state smaller yet. The hfs of the ground state was first resolved by Schüler,[3] using a hollow cathode discharge tube and a Fabry-Perot interferometer. In the next few years there were several attempts to find the nuclear moments of ^{23}Na, from the hfs of certain lines of the Na II spectrum as well as of the *D*-lines.[4-7] This work has been reviewed;[8,9] its accuracy was limited by the Doppler width of the lines, which, even in a liquid air-cooled hollow cathode discharge run at a current of a few ma., is nearly equal to the $^2S_{1/2}$ splitting and about five times as large as the $^2P_{1/2}$ splitting. The latter was resolved only by the use of a collimated atomic beam as source, in emission by Meissner and Luft[10] and in absorption by Jackson and Kuhn.[11] The splittings obtained were:

$$\Delta\nu\ (3^2S_{1/2}) = 0{\cdot}0592\ \text{cm.}^{-1} \qquad \Delta\nu\ (3^2P_{1/2}) = 0{\cdot}0064\ \text{cm.}^{-1}$$

The same technique was applied to resolve the strong field Zeeman pattern, from which the spin value $I = 3/2$ could be obtained unambiguously.[11] The later work on optical hyperfine structure in the alkalies has been reviewed.[12,13]

Other branches of optical spectroscopy have been applied to determine the nuclear moments of ^{23}Na: the spin has been found from the alternation of intensities in molecular bands,[14,15] and the magnetic moment has been estimated from the polarization of resonance radiation in a magnetic field.[16,17,36]

In a magnetic field the hfs of the Zeeman effect in the D-lines has been resolved, as already mentioned,[11] but even when unresolved it has an effect on the Zeeman pattern.[16,17,36,37] With an atomic beam in absorption, the hfs in the Stark effect has also been observed in the D-lines; a quadratic shift in both lines together with splitting of the π- and σ-components in the D_2 line have been measured,[38-40] and the effect treated theoretically.[41]

The most accurate measurements of nuclear moments and of the hfs and Zeeman levels of the ground state have been made by radiofrequency methods, mostly in atomic and molecular beams.[1,2,48] A microwave absorption method for the Zeeman effect has also been described, however,[45,46] and very precise measurements of the magnetic moment of the ^{23}Na nucleus have been made in the solid state by the nuclear magnetic resonance technique.[28-31] The spin[18] and magnetic moment[19] of ^{23}Na were early obtained from atomic beam deflections. Later Rabi's magnetic resonance technique was applied to molecular beams of ^{23}Na to measure the nuclear magnetic moment with greater accuracy[20,22] and to atomic beams to measure the ground state hfs.[21,24] The latter has been compared with the ground state hfs in the other alkali metals and in certain other elements in connection with a very accurate determination of the absolute gyromagnetic ratios of the electron and the proton.[23-25] Atomic beam magnetic resonance experiments have also been performed with the two radioactive isotopes ^{22}Na[26] and ^{24}Na,[27] in which the spins and ground state hfs have been measured and the magnetic moments calculated therefrom.

Recently Rabi *et al.* have succeeded in performing atomic beam magnetic resonance experiments with alkali metal atoms in excited ^{2}P states, and from transitions between hyperfine levels of the $3^2P_{3/2}$ state of ^{23}Na have found a value for the nuclear electric quadrupole moment of $0{\cdot}1 \times 10^{-24}$ cm.^{2}.[34] The magnetic dipole interaction in both 3^2P states has also been measured.[34]

Another very recent technique which has been applied to ^{23}Na is that of magnetic double resonance, in which radiofrequency transitions between hyperfine levels are detected by optical methods. The hfs of the $3^2P_{3/2}$ state has been investigated by this method and a value for the quadrupole moment found in good agreement with that quoted above.[33,35] With this technique a number of experiments have been performed on sodium atoms oriented by changing the populations of the ground state hyperfine levels,[32,42-44] and multiple quantum transitions have been observed.[32]

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Calculations

Early attempts to calculate the energy levels of the sodium atom were made both by adapting Bohr's simple theory[1,2] and by following up iso-electronic sequences,[3-5] a method also applied to doublet separations.[8] Semi-empirical formulæ were used to calculate doublet separations as well.[6,7] Transition probabilities were estimated from the correspondence principle.[2,9] Far more reliable calculations became possible, of course, with the development of quantum mechanics, but semi-empirical formulæ are still applied to certain problems.[10,42]

The application of quantum mechanics to the determination of atomic energy levels and eigenfunctions (and hence transition probabilities) has been fully described by Condon and Shortley.[11] Hartree in 1946 summarized the calculations carried out up to that date on the spectra of the light and certain heavy atoms for states of ionization up to the fourth.[12]

Solutions of the Hartree self-consistent field equations incorporating exchange terms were found for sodium by Fock and Petrashen[13] and later re-calculated by Hartree.[14] Energy levels for several excited states of Na I have been calculated by various treatments of the self-consistent field,[15,16,44] including allowance for polarization of the core electrons.[17,18] Hartree–Fock wave functions have also been computed for several states of Na II,[13,14,43] and

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tables of parameters given for analytic wave functions of the ground and a few excited states of most of the ions Na II to Na X.[19-21,45,49] Calculations of wave functions and energy values for the negative ion Na^- indicate that it should be stable, with an electron affinity in the neighbourhood of +1 eV.[22,23,38,47,48]

Several explanations have been given of the inversion of the ^2D and ^2F terms of sodium and the heavier alkali metals; it is generally ascribed to perturbations by excited states of the core electrons.[24-28] The ^2P intervals have been calculated with Hartree-Fock wave functions.[29,30]

Transition probabilities have been calculated from Kramers and Hartree central fields for lines of the principal series.[31-33] Later calculations for lines of all series have made use of Hartree-Fock wave functions with various approximations.[17,18,34] Intensity calculations have also been made for the two most important 'forbidden' series in sodium, $3s - nd$[39,40] and $3s - np$.[41]

Several calculations of the continuous absorption coefficient as a function of wave-length have been made,[35-37,46] of which the most recent,[37,46] using Hartree-Fock functions, have been compared in some detail with the experimental results. The continuous absorption coefficients of Na^- ions have also been calculated.[38]

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Pressure Effects and Fluorescence

Pressure Effects.

General accounts of the effects of pressure on spectral lines are given in text-books[1,2] and in the review articles written in 1936 by Margenau and Watson[3] and in 1957 by Ch'en and Takeo;[4] both the latter contain many references to work on alkali metal spectra, which have been among the most extensively studied, and accounts of the theories of pressure effects. More detailed theoretical papers have also been published on both foreign gas broadening[5-9] and resonance (self-pressure) broadening.[10,11] The subject is treated briefly here, in view of the availability of review articles.

Several measurements have been made of the broadening and shift of the sodium *D*-lines in absorption in the presence of various foreign gases,[12-15,34] and the observed line contours have been compared with theoretical contours.[15-17] A number of measurements have also been made on higher members of the principal series. The shift is proportional to the relative density of the foreign gas and approaches a constant value at the series limit, while the line width starts to decrease again in the higher members.[18-25]

The appearance of bands near the absorption lines of sodium in the presence of foreign gases has been attributed to the formation of loosely bound polarization molecules of Na_2.[26-30]

Many early measurements were made on the shape and width of the absorption profile of the *D*-lines as the pressure of sodium vapour was increased, and the results compared with those calculated from dispersion theory.[31-42] Later experiments with instruments of greater resolving power and with a wider range of pressure have shown the half-width of the *D*-line to increase linearly with vapour pressure.[43-45]

Fluorescence.

Fluorescence and resonance radiation have been discussed by Mitchell and Zemansky.[1] Resonance radiation in sodium has been excited by lines of sodium[46] and mercury[47] and bands of Na_2.[48-50] Special light sources for the purpose have been described.[51,52,56] Absorption,[53,54] Doppler broadening,[50,55,69] and the relative intensities of the *D*-lines[56,70,73] have been studied in fluorescing sodium vapour, and so also have various phenomena, including line broadening, which appear at high pressures.[54,60,71,72]

Measurements on the quenching of resonance radiation have been made and applied to the calculation of collision probabilities.[56-63,70,74]

The polarization of the resonance radiation has been studied with reference to its dependence on the polarization of the exciting light and the effect on it of magnetic fields of different strengths.[64-72]

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Astrophysics

Investigations of sodium radiation, especially of the *D*-lines, have been of considerable importance in the study of the upper atmosphere and in solar and stellar physics. General accounts of these subjects may be found in various review articles;[24,141-144] only those aspects in which the sodium spectrum plays a part are considered in this brief summary.

The light of the night sky shows emission of the *D*-lines,[1-30,97-110] strongest at twilight and at dawn,[11,14,19,24,25] and the red doublet which is the second member of the sharp series has also been identified.[103] The emission is from a layer variously estimated as between 60 and 120 km. high[14,17-22,24,30,97,106,110] and has been attributed to various dissociation processes involving chlorine or oxygen,[3,4,6,23,30,98,100] to chemiluminescence,[25,27] to ionic impacts,[16] and to absorption of resonance radiation.[14,18,29] A seasonal variation has been noted.[15,24,105] The much fainter radiation between the twilight and dawn bursts is believed to come from a higher layer[20,21,99,110] and is probably excited by a different process.[99,107] The presence of the *D*-lines in the spectrum of the aurora borealis has been reported,[26,108,111,112] but not confirmed.[109,110] Their appearance in the spectra of meteors[31-34,113,114] and comets[35,36] has been attributed to the presence of sodium atoms in the atmosphere;[33] attempts have been made to measure the absorption directly[28,115] and to vary the concentration by injecting sodium vapour from high altitude rockets.[116]

In solar spectroscopy much of the work on sodium has been concerned with observations of the *D*-lines,[37,39,42-45,47,50-53,55,121,122,124] but other transitions have also been identified,[38,46,48,49,54,117-121,123] many of them in the infra-red region, and the possibility of ionization continua has been examined.[41] There is no evidence for the presence of sodium hydride.[40] The appearance of the *D*-lines in solar eruptions has been noted,[44,51] and a considerable number of measurements has been made of their intensities and line profiles in normal conditions and the way in which these vary from centre to limb.[39,43,45,50,52,53,55,121,124]

The possible presence of sodium in the planet Jupiter has been discussed.[56] Sodium lines appear both in emission and in absorption in many stellar spectra,[57-84,89,125-135] including those of certain novae,[67,75,80,83] and again the *D*-lines have been particularly studied for the information they can give on the physical conditions in which they were emitted or absorbed.[57,60,63,64,72,73,130,135] Sodium is also present in inter-stellar gas,[60,85-96,136-140] as free atoms and also perhaps as sodium hydride.[89,90] Various estimates have been made of the amount of sodium present in interstellar gas and of its ratio to other elements.[85-88,93,94,139,140]

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X-Ray Spectrum

Early work on the *X*-ray spectrum of sodium was principally concerned with measurements of the *K*-series lines[1,2,6,7,9,11,12,14,18] and absorption edge;[5] the effect on the latter of chemical combination;[6,20,21] and the *L*-series lines[3,4,12] and edge.[3,4] Some calculations were made on absorption edges and line spectra.[10,13] With better resolution satellites were found near many emission lines; these appear to originate in atoms in which a second electron has been knocked out of an inner shell, either by electron bombardment or in an Auger process.[15,17]

In more recent investigations of the *L*-emission spectrum, broadening and anomalous intensities in certain lines have been ascribed to the Auger effect.[22,24] Very soft *X*-rays due to transitions between different sub-levels of the *L*-shell have been measured.[28] Some quantum-mechanical calculations on *X*-ray levels of sodium have been made.[16,32] Recently a table of energy levels has been compiled from *X*-ray frequencies for sodium and other light elements.[42]

Other effects studied include the Compton scattering of *X*-rays by sodium atoms;[34-37,40] *X*-ray emission from gaseous sodium;[3,4,8] and the mass absorption coefficient, which has been compared with that to be expected from photoelectric absorption and scattering,[39] while the energy distribution of the photoelectrons has also been measured.[33]

With the higher resolution now used in *X*-ray spectroscopy it has been shown that the absorption edges of atoms in the solid state have a fine structure and that, owing to the influence of unbound electrons and neighbouring atoms, many of the emission lines are in fact bands of varying width. Study of these emission and absorption bands gives valuable information about the electronic energy bands in the crystal lattice or the metal as the case may be. Much work has been done on the *K* and *L* edges of sodium, both in crystals[23,29,31,43] and in the metal.[42,43,47] Many measurements have also been made on the emission bands from sodium metal and their relation to the free electron conduction bands,[19,24-27,30,41] and some calculations on the subject have been made.[32,38,47]

Another recent development in *X*-ray spectroscopy is the production of so-called mesonic *X*-rays (*i.e.*, *X*-rays from an atom in which the radiating electron is replaced by a meson). Information can be derived about both the atomic nucleus and the meson. In sodium, *K*- and *L*-series lines have been identified from π-mesonic atoms.[44,45,46]

A number of reviews discuss the *X*-ray spectrum of sodium, with particular emphasis on the importance of *X*-ray spectroscopy in solid-state physics.[48-50]

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THE MOLECULAR SPECTRA OF SODIUM AND CERTAIN OF ITS COMPOUNDS

By R. F. BARROW

The Sodium Molecule

The spectrum of the sodium molecule, Na_2, stretches from the near infra-red to the ultra-violet. It may be observed in absorption,[1,6,8] and in emission in fluorescence,[1,3,5,23,27,29] excited by active nitrogen[12] or in discharge tubes.[4,22,26] The magnetic rotation spectrum has also received a good deal of attention.[7,14,18,19,28,32] Values of the molecular constants are collected in Table IV.

TABLE IV. - SPECTROSCOPIC CONSTANTS FOR Na_2

State	T_0	ω_e	$x_e\omega_e$	$y_e\omega_e$
F	35530·$_3$	106·2	0·65	–
E	33462·$_6$	111·3	0·48	–
D	31930	112	0·7	–
$C^1\Sigma_u^+$	29322·1	119·33	0·53	–
$B^1\Pi_u^+$	20302·5	123·79	0·6303	–0·00936
$A^1\Sigma_u^+$	14659·7	117·6	0·38	–
$a^3\Pi_0{+}_u$	<14660	~145	–	–
$X^1\Sigma_g^+$	0	159·23	0·726	–0·0027

State	B_e	α_e	r_e, A.
C	B_2 = 0·103	–	3·7$_7$
B	0·12588	0·00094	3·413$_0$
A	0·1107	0·00054	3·63$_9$
a	~0·140	–	–
X	0·15471	0·00079	3·078$_6$

Notes.
1. The constants for the upper states D, E and F are uncertain.
2. The constants for the state $a^3\Pi_0+$ have been determined from a study of the perturbations with $A^1\Sigma^+$.
3. For earlier analyses, see [2,9,15].

The red[6,11,13,14] and blue-green[6,7,10,19] systems, A–X and B–X respectively, are the best known. The C–X system[33,34,36] now seems satisfactorily analyzed, but there is little agreement between the arrangements proposed for the bands at shorter wave-lengths.[21,30,31,35,37,39]

The observation of a magnetic rotation spectrum in the region of the $A^1\Sigma_u^+$–$X^1\Sigma_g^+$ transition is interesting and unexpected. It proves to arise from a perturbation of specific rotational levels of the $A^1\Sigma_u$ state by a state $a^3\Pi_0{+}_u$, and the analysis of the effect yields values for the rotational and vibrational constants of the perturbing triplet state.

The magnetic rotation spectrum also leads to information about the positions of highly excited vibrational levels in state $B^1\Pi_u$. These may be extrapolated to a dissociation limit at 23120 cm.$^{-1}$ This limit corresponds to dissociation into one normal (3^2S) and one excited (3^2P) sodium atom, and subtracting the energy of atomic excitation, $D_0''(Na_2)$ = 17·59 kg.-cal. mole.$^{-1}$ Since it is possible[43] that there is a low potential maximum in the upper state, this estimate may be a little high. Molecular-beam experiments[40] give, when recalculated,[42] D_0'' = 16·91 kg.-cal. Observations on dilute flames of sodium vapour and bromine or mercuric bromide give[41] D_0'' = 18·5 kg.-cal. Measurements of the vapour pressure of sodium are consistent[42] with $D_0'' \sim 19$ kg.-cal. The two latter estimates are less reliable than the former, and the 'best' value seems to be D_0'' = 16·9$_1$ ± 0·35 kg.-cal.

Measurement of the relative intensities in successive rotational lines of the B–X system show that the nuclear spin of ^{23}Na is $\frac{3}{2}$, and that it obeys Fermi–Dirac statistics.[17,45,46]

A calculation has been made of the absolute strength of the A–X transition.[38] The relative strength of bands in the B–X system has been discussed.[16] Measurements have been made of the degree of polarization of lines in the fluorescence spectrum.[44]

Apart from the systems of bands with discrete structure, a number of bands arising from weakly-bound polarization molecules have also been observed.[20,24,25] A continuous emission spectrum has been examined,[47] and diffuse absorption[48,49] and emission[50] bands attributed to weakly bound molecules Na–X, with X = Mg,[48] Zn,[49] Cd,[49] Hg,[49] and Xe.[50]

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The NaK Molecule

The spectrum of the NaK molecule may be readily observed, either in absorption[1,2,4–12] or in fluorescence.[2,5] The spectroscopic constants are given in Table V. Magnetic rotation spectra have also been observed,[10] not only, as expected, in the systems for which a noticeable Zeeman effect is predicted,[13] but also weakly in the system $A^1\Sigma^+ \leftarrow X^1\Sigma^+$ (for an interpretation of this effect in the cases of Na_2 and K_2, see [14]). However, in the green bands of NaK(C–X) it has not apparently been possible to find any correspondence between the absorption and magnetic rotation spectra.[10] The dissociation energy may be obtained by an extrapolation of the vibrational levels in state $C^1\Pi$, which correlates with $Na(3^2P) + K(4^2S)$: thus $D_0''(NaK) = 14{\cdot}3$ kg.-cal. mole.$^{-1}$

TABLE V. - SPECTROSCOPIC CONSTANTS[10,12] FOR NaK

State	T_0	ω_e	$x_e\omega_e$	$y_e\omega_e$
$D(^1\Sigma^+)$	25214	95·85	0·94	–
$C^1\Pi$	20070·0	82·17	0·350	−0·00814
$B^1\Pi$	16965·8	72·60	1·475	+0·2436*
$A^1\Sigma^+$	12118·1	79·85	0·0872	−0·003887
$X^1\Sigma^+$	0	123·29	0·400	–

* $-0{\cdot}000545(v + \frac{1}{2})$.[4]

Note. Earlier analyses[3,9] are incorrect.

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The NaRb Molecule

Bands attributed to this molecule have been observed in absorption.[1] The magnetic rotation spectrum has also been examined.[2] The molecular constants are listed below.

Refs. p. 1376

State	T_0	ω_e	$x_e\omega_e$
B	(18600)*	(62)*	-
$A^1\Pi$	16399·1	61·49	0·945
$X^1\Sigma^+$	0	106·64	0·455

*The analysis[3] of the bands of the B–X system is doubtful.

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The NaCs Molecule

Bands of this molecule have been observed in absorption under low dispersion.[1] The analyses[2] are uncertain.

State	T_0	ω_e
C	(24250)	(62)
B	(18233)	(65)
$X^1\Sigma^+$	0	(98)

References

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2 Weizel, W. & Kulp, M., *Ann. Phys.*, 1930,[5],**4**,971-84. (*24*,3434)

Sodium Hydride

The spectrum of sodium hydride is readily observed, both in emission and absorption. The rotational analysis of a number of bands has been carried out:[1-4] the results are confirmed by the analysis of some of the deuteride bands.[3] Constants are given below. For a discussion of the spectra of the alkali-metal hydrides, see reference 5 and LiH (see page 284). An emission continuum has also been reported.[6]

State	T_e	ω_e	$x_e\omega_e$	$y_e\omega_e$	D_0, kg.-cal.
$A^1\Sigma^+$	22719·1	310·6	-5·41	-0·197*	-
$X^1\Sigma^+$	0	1172·2	19·72	+0·160*	47·$_3$ ± 5

State	B_e	α_e	r_e, A.
$A^1\Sigma^+$	1·696	-0·0175*	3·20$_8$
$X^1\Sigma^+$:NaH	4·9012	0·1353	1·8873
$X^1\Sigma^+$:NaD	2·5575	0·0520	1·8865

*Further terms known.

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Sodium Halides

The spectra of the sodium halides in absorption in the vapour state have been investigated as follows:-

Microwave region: sodium chloride,[1,14] bromide[1] and iodide.[1]
Infra-red(vibration-rotation) region: sodium chloride,[2] bromide[2] and iodide.[2]
Electronic spectra: sodium fluoride,[3,4] chloride,[3,8] bromide[3,5,8] and iodide.[5-8]

Values of the molecular constants for these molecules are collected in Table VI, together with the thermochemical information required for the determination of their energies of dissociation (see also page 282).

TABLE VI. - SPECTROSCOPIC CONSTANTS FOR THE GASEOUS SODIUM HALIDES

Molecule	B_e	α_e	r_e, A.	ω_e, cm.$^{-1}$	μ, D.
NaF	-	-	[1·840]	[500]	-
NaCl	6537·07$^{(2)}$	48·28$^{(2)}$	2·3606	366	8·5 ± 0·4
NaBr	4534·52$^{(3)}$	28·25$^{(3)}$	2·5020	302	-
NaI	3531·78	19·44	2·7115	258	-

Notes.
1. The values of B_e, α_e, r_e and μ are taken from reference 1. The values for B_e and α_e are in Mc./sec. Values of ω_e are from reference 2.
2. Constants for $Na^{35}Cl$.
3. Constants for $Na^{79}Br$.
4. The figures in square brackets are estimated values.

Dissociation Energies, D_{298}, kg.-cal. mole.$^{-1}$

	NaF	NaCl	NaBr	NaI
$-Q_f(MX)$	136·3^{a}	97·755^{e}	86·03^{e}	68·84^{e}
$-\Delta_s H(MX)$	-67·3$_5$^{b}	-56·24^{f}	-53·6^{f}	-52·3^{f}
$\Delta_s H(M)$	25·86^{c}	25·86^{c}	25·86^{c}	25·86^{c}
$Q_f(X)$	18·86^{d}	29·01^{e}	26·71^{e}	25·48^{e}
D_{298}	113·7	96·39	85·0	67·9

Notes.
a reference 9.
b reference 10.
c reference 11.
d recalculated, from reference 20.
e reference 12.
f reference 13.

The observation[14] of the Stark pattern of the line $J = 1 \rightarrow 2$ in the microwave spectrum of sodium chloride leads to the value $\mu = 8·5 \pm 0·2$ D. for the dipole moment. Spectra in the radiofrequency region corresponding to transitions $m_I = \pm 1$, $m_J = 0$ for both Na and Cl have been studied at magnetic fields between 2000 and 16000 gauss in a molecular beam[15] of sodium chloride. The spectra are more complicated than is expected for a diatomic molecule, and it is suggested that the beam contains dimers, $(NaCl)_2$. Similar effects were observed with sodium fluoride and sodium iodide. Other observations on the low-frequency molecular beam resonance spectra have been reported for sodium fluoride,[16,18] chloride,[16-18] bromide[16,17] and iodide.[16,17]

The velocity distribution among excited sodium atoms formed by the photodissociation of sodium iodide has been studied in connexion with the quenching of the sodium fluorescence by foreign gases.[19]

Refs. p. 1378

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SODIUM AND SODIUM COMPOUNDS: SOLID STATE

Sodium

Films of sodium deposited on fluorite at liquid air temperatures are transparent in the Schumann region[1] (see also [2-5]).

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Sodium Hydride

The absorption spectrum of thin films of sodium hydride, deposited on quartz, has been investigated in the ultra-violet region.[1] An absorption maximum occurs at 2000A.

Reference

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Sodium Oxide, Na_2O

The absorption by thin films of sodium oxide deposited on quartz has been investigated in the ultra-violet region.[1] Maxima are observed at 2800, 2100 and (1870) A. The position of the longest-wave-length absorption band is related to the Coulomb part of the lattice energy, the electron affinity of oxygen and the ionization potential of sodium (see page 285).

Refs. p. 1379

Reference

1 Rauch, W., *Z. Phys.*, 1940,**116**,652-6. (*35*,4682)

Sodium Hydroxide

The infra-red spectra of solid NaOH, NaOD and of mixtures of the two have been examined,[1] both at room temperature and at liquid-air temperature. The results are interpreted in terms of a structure in which the unit cell contains two sodium hydroxide molecules related to each other by centres of symmetry.

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Sodium Halides

In order to avoid repetition, certain properties of the crystalline alkali metal halides are discussed in detail under only one appropriate alkali metal, as follows: ultra-violet absorbtion spectra, page 285; Raman spectra, page 1380; colour centres, luminescence and phosphors will be considered under Potassium in the next Supplement(Volume 2, Supplement 3, The Alkali Metals, Part 2.)

Absorption maxima of the sodium halides lie at the following wave-lengths[1] in the infra-red:-

NaF, 40·5 μ; NaCl, 61·1 μ; NaBr, 74·7 μ; NaI, 85·5 μ;

(For a theoretical study of the infra-red vibrations in sodium chloride, see [18]). In the ultra-violet region, the crystals show absorption maxima[2-4,21] as follows:-

NaF	1170A.				
NaCl	1580	1280A.			
NaBr	1880	1760	1450	1250A.	
NaI	2280	1870	1700	1410	1220A.

The absorption spectrum of sodium chloride has been observed[5] in the vacuum ultra-violet region as far as 400A. by the (heroic) method of distilling halide on to the spectrograph grating. The absorption spectra of the molten halides have also been examined.[6]

Sodium chloride is of great importance as an optical material for infra-red spectroscopy,[10] especially in the region 8 to 15 μ. Measurements of its refractivity[7,8] and of its transmission[9] are available (see also [11-13]). Coatings designed to protect rock salt lenses against the action of water have been described.[22] The diffuse reflectance of finely divided packed powder has been measured[14] from 0·8 to 20 μ, and the use of sodium chloride in filters for the region 30 to 43 μ has been discussed.[15] Absorption lines arising from crystal imperfection have been observed[20] for rock salt in the region 150 to 350Mc./sec.

The structure of the infra-red band at 3 μ of sodium bromide dihydrate has been examined[16] and the Raman spectrum of a single crystal has also been studied.[17] The interpretation of the results leads to a suggested orientation for the water molecules in the crystal.

Enolization in solutions of sodium iodide in acetone has been studied by observations of their infra-red and Raman spectra.[19]

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Raman Spectra

The homogeneous vibration of the alkali-halide crystals is active only in the infra-red spectrum, and no first-order Raman spectrum appears. There is, however, a second-order Raman spectrum[1] which in the alkali halides arises through the electrical anharmonicity of the vibrations.[2,3] Two quite different views of the nature of the vibrations of a crystal lattice have been put forward, one based on the work of Born and von Kármán, the other on a theory advanced by Raman (for a review, see Menzies[4]). The present evidence seems to favour the earlier ideas. References to other theoretical and experimental work on the Raman effect in the alkali halide crystals are given below.[5-27]

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Sodium Sulphate

The Raman spectra of single crystals of thenardite and of Glauber's salt have been obtained.[1] Infra-red absorption bands in the region 1·3 to 2 μ of the latter salt have been examined,[2] as has the nuclear paramagnetic resonance absorption for protons.[3] Details of the infra-red powder spectra have been given.[4]

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Sodium Carbonates

The infra-red spectra of sodium carbonate, sodium sesquicarbonate and sodium bicarbonate have been studied by the powder method.[1] There is a large shift in the O–H stretching vibration from the normal value of 3700 cm.$^{-1}$ to 2440 cm.$^{-1}$ in sodium bicarbonate,[2] indicative of very strong hydrogen bonding.

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Sodium Nitrate

A number of observations of the Raman effect in crystals of sodium nitrate have been made.[1-6,9,12] The spectrum changes somewhat with temperature[3] and on fusion.[3-5,9] Frequencies have been assigned to lattice and to ionic motions in the crystal.[5] The spectrum has also been photographed at different orientations of the crystal relative to the directions of illumination and of observation with different states of polarization of the incident light.[6,7] A force-constant treatment has been given.[8] The infra-red absorption[10,11] and reflexion[12] spectra have also been observed, and the relation between these spectra and the Raman spectrum has been considered.[12] The infra-red spectra of samples containing 50% of the nitrogen content as ^{15}N have been examined, and the shift of the perpendicular bending frequency discussed.[16] From the effect of temperature on the lines at 100 and 190 cm.$^{-1}$ it is concluded[13] that there is free rotation of the nitrate ion about the ternary axis above the transition point at 275°. The infra-red frequencies of the nitrate ion are somewhat lower in aqueous solution[15] than in the crystal.

The Raman spectra of mixed crystals of sodium and potassium nitrates[14] have been studied.

Refs. p. 1382

The absorption spectrum of the crystal in the ultra-violet region has been examined.[17,18] The crystal has an absorption maximum at about 2960A., where the molecular absorption coefficients are 1200 and 16000 parallel and perpendicular to the c axis, respectively. Since the absorption is chiefly due to the nitrate ions, and since these lie perpendicular to the c axis, the coefficients represent the gram-ionic coefficients of the nitrate ion.[17]

Changes in the absorption spectra of sodium nitrate crystals on exposure to ionizing radiation (neutrons, γ-rays, X-rays, ultra-violet radiation) have been investigated.[19] The main effects arise from (a) the conversion of nitrate ions into nitrite ions with an absorption peak at 3450A., and (b) the production of colour centres giving a continuous absorption band with a maximum at 3350A.

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Sodium Phosphates

The powder method has been used to determine the infra-red absorption spectra of sodium trimetaphosphate[1] and of a number of other sodium phosphates.[2] The Raman spectra of the hydrates Na_2HPO_4,nH_2O with n = 2, 7 and 12 have been examined.[3]

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SECTION XL

THE ANALYTICAL DETERMINATION OF SODIUM

By H. V. THOMPSON

DETECTION

The ready solubility of most sodium salts in water, coupled with the ease of application and sensitivity of the flame test, has militated against the detection of sodium by wet tests to such an extent that in the past reliance has been placed mainly on the sparing solubility of sodium pyroantimonate and dihydroxytartrate. Streng's uranyl acetate test[1] was overlooked for many years, and not until Blanchetière had developed the reaction into the triple acetate method for determining sodium[2] did it become the standard wet test for the element.[3-8] Normally, sodium is precipitated with zinc or magnesium uranyl acetate, but the corresponding cobalt,[9] nickel,[10] manganese[11] and copper[12,13] uranyl acetates have also been recommended.

While many metals and acid radicals do not interfere, the test is usually applied to a solution containing only the alkali metal chlorides, but lithium should not be present in concentrations exceeding about 0·1%[14] or, if present in larger quantities, should be removed from the mixture of anhydrous chlorides by a suitable organic solvent (see page 288). From concentrated solutions of potassium salts a double acetate, $KUO_2(CH_3COO)_3$, is precipitated;[12] consequently with such solutions the bulk of the potassium must first be removed as perchlorate.[15]

Other methods of detection have been based on the formation of a sparingly soluble cæsium bismuth triple nitrite,[16] $NaCs_2Bi(NO_2)_6$, on the bismuth double sulphate, $3Na_2SO_4, 2Bi_2(SO_4)_3, 2H_2O$,[17,18] and on the use of certain organic reagents.[19-22] When present in traces only, sodium is detected spectrographically.

DETERMINATION BY CHEMICAL METHODS

Gravimetric Methods.

In 1883 Streng proposed the use of uranyl acetate as a microchemical test for sodium, but it was 40 years before the conditions for the quantitative precipitation of sodium and a bivalent metal as the triple uranyl acetate were worked out. The limitations and errors of the method, with special reference to the removal of interfering metals and acid radicals, have been widely investigated and the process is now on such a sound analytical footing that it has no rival in the gravimetric field.[23-39,264]

The determination can be completed by drying the precipitate to constant weight or, in special cases, by measuring the volume of the centrifuged precipitate;[40-43] but a volumetric or colorimetric finish is often preferred (see below). The triple acetate technique is highly flexible and has been applied in such widely diverse spheres as the determination of sodium in biological materials,[44-66] aluminium,[67-72] water,[73-80] silicates, cement and ceramic products,[81-96] potassium compounds[97-102] and soils.[98,103-107]

A number of papers has been published containing bibliographies and reviews of methods for the determination of sodium[108-116,265] and, although the majority of these concentrate on the triple acetate process, references will be found to other methods, e.g. determination as pyroantimonate[110,112,117] or triple nitrite,[112,118] which are now of little more than historical interest.

Volumetric Methods.

Volumetric processes for the determination of sodium after precipitation as sodium zinc (or magnesium) uranyl acetate fall into two main groups. In the oxidimetric procedure the uranium in an acid solution of the precipitate is reduced from the hexavalent to the tetravalent state and then reoxidized by titration with a standard solution of potassium permanganate,[119-126] dichromate[127-130] or ceric sulphate.[131,132] Alternatively, the reduction can be effected by adding a measured excess of a standard solution of titanous chloride, followed by back titration of the excess.[133,134]

In the alkalimetric method, an aqueous solution of the triple acetate is titrated with a standard solution of sodium hydroxide,[135-143,265,266] when the reaction under prescribed conditions is represented by the equation:-

$$NaZn(UO_2)_3(CH_3COO)_9 + 9NaOH = NaHUO_4 + 2UO_2(OH)_2 + Zn(OH)_2 + 9CH_3COONa + H_2O.$$

Other methods have also been suggested, e.g. titration of the uranyl salt in the triple acetate with a standard phosphate solution[144,145] and precipitation of uranyl hydroxyquinolinate which is then titrated bromometrically,[146] or titration of zinc in the triple zinc salt with ethylenediaminetetra-acetic acid.[146a] Sodium in aluminium can be determined by titration of the hydroxide after removal of the aluminium as amylate.[146b]

DETERMINATION BY PHYSICAL METHODS

Colorimetry.

Various methods for the colorimetric determination of sodium are based on its prior precipitation as a triple acetate. When the sodium is precipitated with magnesium or zinc uranyl acetate, the comparison is based on the intensity of coloration of a simple solution of the precipitate[147-158,266] or on that after the addition of a reagent whereby a colour is developed. Thus, in acetic acid solution, potassium ferrocyanide gives brownish red potassium uranyl ferrocyanide,[159-174,265] while in alkaline solution hydrogen peroxide produces an intense yellow to red colour,[175-177] and certain organic reagents[178-180] are said to form with the uranyl ion coloured complexes suitable for colorimetric comparison.

If precipitated as sodium manganese uranyl acetate, the sodium is determined indirectly by oxidizing the manganese to permanganate with potassium periodate,[181-183] and with the corresponding nickel salt the nickel is determined colorimetrically with dimethylglyoxime,[184,264] or from the copper salt *via* the cuprammonium ion or dithizone,[184a] while Titan Yellow has been used to determine the magnesium in the triple magnesium salt.[184b]

Colorimetric methods for the determination of sodium have recently been reviewed.[185]

Polarography.

An essential preliminary to the polarographic determination of the alkali metals is the removal of most of the heavy metal ions, either by classical methods or by electrolysis in acid solution with a mercury cathode. Even so, in the residual solution separate determinations of sodium, potassium, rubidium and caesium in the presence of one or more of the other alkali metals is impossible as, owing to the close grouping of their half-wave potentials, a single cumulative wave is given.[186]

In the absence of potassium and with not more than a fifty fold excess of lithium present, sodium can be determined with a satisfactory degree of accuracy in a variety of materials.[186-190]

When potassium is present, a polarogram either succeeded or preceded by a chemical separation of the two elements is normally necessary in order to complete a determination,[191-194] though indirect polarographic methods have been suggested.[195,196]

Flame Photometry.

Flame photometry has proved to be of great value in determining relatively small amounts of sodium in widely different types of materials.[197-211] Because no preliminary separation of the alkali metal salts is necessary, the method is much quicker than any chemical procedure, and the results are at least as accurate as those obtained gravimetrically.

The precise experimental details depend in part on the type of flame photometer used and also on the nature of the material under examination, e.g. with minerals and silicates a working solution has first to be obtained by evaporation with hydrofluoric and sulphuric acids. Again, with a normal clay, low in lime and high in alumina, an interference filter reduces any error due to the presence of lime to insignificant proportions, whereas several other procedures have been adopted to the same end for other materials.[212-218]

An additional advantage of the method is that not only potassium, but also lithium, can be determined in the same solution, as, in some analyses of silicates by the classical procedure, flame photometry has revealed that lithium oxide has been included in the reported figure for sodium oxide.[219]

Another fruitful application of flame photometry is in the determination of sodium and potassium in biological materials.[220-234] Recent literature on the flame photometric determination of the alkali metals includes several reviews.[234a]

Spectrography.

Arc, spark or flame excitation can be used for the spectrographic determination of sodium and in general there is no overriding factor which singles out any one procedure for special consideration. Thus, all three techniques have been applied to the determination of sodium in aluminium and aluminium alloys,[235-243] and in minerals, rocks, clays, cement,[236,244-250] biological materials and soils.[251-261] Visual examination of the spectra has also been applied on a quantitative basis.[262]

Though spectrography is particularly useful for the examination of small samples, as in biological work or in materials with only minor to trace quantities of sodium, it is not necessarily limited to the lower end of the scale, and by using a d.c. arc it has been found that in the analysis of silicates the range can be extended with satisfactory accuracy up to amounts of sodium of the order of 7%.[263]

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SECTION XLI

BIOLOGICAL PROPERTIES OF SODIUM

By F. CALL

Introduction

Sodium salts are found almost everywhere in nature and are extremely important in biology. Thus sodium chloride occurs in the internal fluids and intracellular juices of almost all living organisms. Like most minerals normally present in biological systems, the internal concentration is closely regulated and since the inevitable losses must be replaced, sodium is an essential element for life. Usually there is an optimum daily intake below which growth of the organism suffers while a very high concentration or excessive intake may be toxic, producing disorders or even death. It is difficult to discuss the biological properties of sodium without some reference to potassium, for the two exhibit what has been termed 'biological antagonism'. Thus most cells, plant or animal, maintain a definite balance between the two elements and usually the interior of the cell has a higher content of potassium, sodium being largely excluded, while the cell membrane often exhibits very different permeabilities to the two ions. Very often much work has to be performed to transport sodium out of the cell and the mechanism of this 'active transport' is still unexplained. There are several useful reviews of recent literature on the biological antagonism of sodium and potassium.[1-3]

The present review is based on a selection from many thousands of references, and most articles of a purely medical nature have been excluded. While an effort has been made to restrict discussion to the biological properties of the sodium ion, it is not always possible to discriminate between the effects of the cation and those of the anion. Most of the common salts of sodium, the chloride, hydroxide, nitrate, sulphate etc., have therefore been included when it was clear that the anion did not play the dominant role.

This very wide field necessitates the subdivision of the subject under the following headings:

1 Occurrence and use in food.

2 Preservative and stabilizing action.

3 Sodium and micro-organisms (including bacteria, moulds, fungi, yeasts, viruses and phage).
    i Tolerance and requirements
    ii Effects on activity and products
    iii Bactericidal action
    iv Metabolic effects
    v Morphological effects
    vi Effects on permeability of cell wall.

4 Sodium and plant growth.
    i Occurrence in soils
    ii Sodium salts as fertilizers
        (a) sodium chloride
        (b) sodium nitrate

iii Occurrence and distribution in plants
iv Requirements of plants for sodium
v Tolerance of plants to sodium
vi Physiological effects
(a) General
(b) Interaction of ions.

5 Sodium and marine or freshwater organisms.
i Requirements, tolerance and distribution
ii Permeability and ionic regulation
iii Specific biological effects.

6 Sodium and invertebrates.
i Insects
ii Helminths

7 Sodium and mammals.
i Growth requirements
ii Toxicity
iii Distribution in animal and human tissues
iv Metabolism
v Sweat and temperature regulation
vi Excretion
vii Specific biological effects on
(a) the whole organism
(b) muscle
(c) nerve conduction
(d) active transport
(e) permeability of tissues
(f) proteins.

8 Effect on Enzymes.

Occurrence and use in foods

The sodium contents of common foods have recently been reviewed.[4,5] Milk contains about 3g. of sodium chloride per quart.[6] The sodium content of meat varies widely both in different kinds of meat and in individual specimens of the same kind, mean values ranging from 70mg. per g. in beef muscle to 159mg. per g. in beef liver and kidney.[7] The sodium content of frozen green vegetables also shows wide variation from 1·26mg. per 100g. in green beans to 151·9mg. per 100g. in Lima beans.[8] English beer contains between 0·17 and 0·31g. of sodium chloride per pint,[9] while up to 200p.p.m. (about 0·100g. per pint) of sodium chloride in the water used for brewing American beer is regarded as having a desirable effect on the taste.[10] The use of sodium chloride in baking bread has been reviewed[11] and measurements have been made of the effect on the consistency of the dough.[12] It is important to obtain the correct content and distribution of sodium chloride in cheese-making, the salt serving to regulate the consistency, the water content, the flavour and the growth of bacteria.[13-19] Sodium glutamate is now widely used in food processing and the correct proportion of sodium chloride must be present to ensure the optimum flavour.[20] The radioactivity produced by neutron irradiation of the sodium contained in foods is not regarded as affording a serious hazard on ingestion.[21]

Preservative and stabilizing action

Sodium chloride is universally used for preserving foods. The preservative action on meat is due partly to dehydration and partly to a selective action on the bacteria and other micro-organisms contaminating the meat. Although putrefaction may be supressed, anaerobic fermentation may proceed with subsequent development of an agreeable flavour.[22-24] The salting of fish may become more difficult when the fat content exceeds 2%, possibly because of reduced penetration of the salt.[25] The oxidation and subsequent rancidity of fats may be promoted by the presence of iron as an impurity in common salt.[26] Although many vegetables have a satisfactory flavour and consistency after storage in brine[27-30] there are heavy losses of carotene and ascorbic acid after a few months[31,32] in spite of the fact that common salt has an inhibiting effect on the oxidation of ascorbic acid.[33] This inhibition results in a higher ascorbic acid content in vegetables cooked in salt water,[34-36] but is opposed by acidity so that salads treated with dressings and orange juice containing common salt rapidly lose ascorbic acid.[33,37] Sodium chloride had no effect on the rate of loss of thiamine caused by cooking[38,39] nor on the decomposition of vitamin A in liver oil.[40,41] Sodium bicarbonate halves the cooking time of peas but has no effect on the thiamine, riboflavin or ascorbic acid content.[42] Bacterial spoilage of cream[42] and cheese[44] is reduced by the addition of common salt. Sodium chloride accelerates the rate of decomposition of aqueous adrenaline hydrochloride.[45]

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Effects of Sodium Salts on Micro-organisms

(i) Tolerance and Requirements

Micro-organisms show great differences in their response to sodium salts, growth being in general stimulated by low concentrations and inhibited by higher concentrations. The most commonly studied salt has been sodium chloride and Table I shows the tolerance of a number of species of bacteria, moulds and yeasts to this substance. Concentrations have been rounded off and converted where necessary to the most frequently used unit, % (g. per 100ml.). Since many factors such as pH, temperature, nature of the medium, etc., affect the tolerance, these figures must be taken as only a rough guide to the relative susceptibility of micro-organisms to sodium chloride. Different strains of the same organism may also show differences in tolerance. Nevertheless it is quite clear that there are very wide characteristic differences between different species.

The difference in the relative susceptibilities of different species has been used to obtain pure cultures of certain organisms. Thus pathogenic strains of staphylococci can be obtained free from non-pathogenic contaminants by adding 7% of sodium chloride to the medium.[18,35]

A definite requirement for sodium has been demonstrated for many micro-organisms[14,23,39-41] and sodium can to some extent compensate for deficiencies of potassium.[42,43]. The stimulating effect of sodium appears to be specific for some species[17,44] but other workers[45,46] have found that other salts can be substituted and they attribute the effect of sodium to the osmotic pressure. Concentrations of sodium chloride as low as 10^{-5}M. protect *Bacillus cereus* against the toxic effects of distilled water.[47] Both the stimulating and inhibiting effects of sodium chloride are dependent on the pH of the culture medium[17,48-52] but the precise relationship appears to vary not only with the species but also with the strain. Thus one strain of a species of propionic acid bacterium occurring in cheese was more susceptible to the salt at a low pH than at a high one but the reverse was true for another strain of the same species.[50] Commercial grades of sodium chloride may contain impurities which cause the pH of solutions to vary with salt concentration and at constant pH increasing concentrations of salt are correlated with the aerobic redox potential possibly caused by a reduction in partial pressure of dissolved oxygen.[53] The susceptibility of organisms has also been found to vary with the nature of the culture medium.[10] Interactions have been found between different cations present in a culture medium, and sodium chloride may either diminish or enhance the

TABLE I.- TOLERANCE OF MICRO-ORGANISMS TO SODIUM CHLORIDE

Species	Concentration g. per 100ml.			Ref.
	Optimum	Tolerated	Inhibitory	
Aerobacter aerogenes	0·5-2·0	-	-	1
Aerobacter aerogenes	-	7·5-8·0	-	2
Aerobacter cloacae	-	8·5-9·0	-	2
Aerobacter cloacae	-	7	9	3
Azotobacter chroöcoccum	0·1	-	3	4
Azotobacter chroöcoccum	-	-	1	5
Azotobacter halophilum	5	-	-	5
Bacillus breslau	-	15	-	6
Bacillus pumilus	10	-	20	7
Clostridium botulinum	-	-	7·8-9·5	8,9
Clostridium butyricum	-	-	1-3	10
Clostridium lentoputrescens	-	-	7·8	8
Clostridium perfringens	-	-	6	11
Clostridium saccharobutyricum	-	-	3	11
Clostridium sporogenes	-	-	7·8-9·5	8
Clostridium sporogenes	-	-	6	11
Clostridium tyrobutyricum	-	-	0·6	12
Debaryomyces sp.	-	24	-	13
Escherichia coli	-	10-15	-	6
Escherichia coli	0·8	-	4·3	14
Escherichia coli	2-3	-	-	15
Escherichia coli	0·3-0·5	-	5-10	16
Escherichia coli	0·6	-	-	17
Escherichia coli	-	-	10	18
Eberthella typhosa	-	3	-	19
Eberthella typhosa	1-2	-	-	15
Klebsiella pneumoniae	2	-	-	15
Lactobacillus acidophilus	2	-	-	20
Lactobacillus brevis	1	-	3·5	21
Lactobacillus bulgaricus	-	-	1	20
Leptospira sp.	-	-	2	22
Leuconostoc dextranicum	0·5-2	-	3	1
Leuconostoc mesenteroides	1	-	-	21
Leuconostoc sp.	-	4	-	40
Micrococcus halodenitrificans	2	-	-	23, 24
Mucor racemosus	-	4	10	25
Mycoderma	-	15	-	12
Oidium lactis	-	8	-	25
Oidium lactis	-	-	1	26
Ophiobolus miyabeanus	-	-	5·8	27
Penicillium anomalum	-	18	-	25
Penicillium baiiolum	-	6	12	25
Penicillium camemberti	-	4	6	25
Penicillium candidum	-	12	-	25
Penicillium chlorophaeum	-	8	10	25
Proteus vulgaris	-	-	10	18
Pseudomonas fluorescens	-	-	1	26
Pseudomonas sp.	1-2	-	5	28
Photobacillus radians	1·8-3·0	-	-	29-31
Salmonella pullorum	-	3	-	19
Salmonella schotmulleri	-	3	-	19

continued on following page

TABLE I continued

Species	Concentration g. per 100ml.			Ref.
	Optimum	Tolerated	Inhibitory	
Salmonella typhi	0·8	-	-	32
Serratia marcescens	1	-	-	26
Staphylococcus spp.	0·5-1	-	-	15
Staphylococcus spp.	-	-	15-20	33
Staphylococcus spp.	-	7·5-15	-	34
Staphylococcus spp.	-	7·5	-	35
Sterigmatocystis nigra	-	-	1-3	36
Streptococcus diacetilactis	0·5-2	-	3	1
Streptococcus lactis	1	-	6	37
Streptococcus lactis	0·5	-	2	1
Vibrio comma	7-8	-	9-11	38
Vibrio spp.	2·0-5·8	-	20	39

toxicity of a particular ion.[5,14,54,56] Micro-organisms have very great powers of adaptation and it is comparatively simple to breed strains capable of tolerating much higher concentrations of salt.[2,4,7,20,57-60] Such adaptation is specific for each substance[19] and, since the statistical chances of developing resistant forms depends on the total number of organisms, the apparent tolerable concentration may vary with the size of the inoculum.[61] It has been observed that both high and low concentrations of sodium chloride are toxic in the lag phase of growth and stimulating in the logarithmic phase so that the actual age of a particular cell may be important.[23,62] The inhibitory effects of sodium chloride may be reversed by the addition of vitamin B_{12}[63,64] and the addition of salt to media is helpful in the assay of this vitamin.[65] Sodium chloride also reduces the toxic effect of ammonium carbonate on urea bacteria.[66] In a number of species of bacteria involved in the lactic fermentation of cucumbers, the tolerance to salt depends on the reduction potential of the solution.[67] The heat resistance of thermophilic bacteria is reduced by sodium chloride.[68-70]

(ii) Effects on the Activity and Products

Sodium chloride is essential for the production of light by luminescent bacteria.[29-31,71-72] This salt inhibits toxin production by *Clostridium botulinum*[73,74] but increases sporulation in *Clostridium tetani*.[75] It also increases the resistance of *Salmonella pullorum* to neomycin[76] but has no effect on that of *Klebsiella* to streptomycin.[77] Strains of *Streptococcus spp.* resistant to penicillin and chloramphenicol are also tolerant to higher concentrations of sodium chloride.[78] Sodium chloride causes pigment formation in cultures of *Serratia marcescens* at a temperature normally inhibitory to this process[79] but pigment production in *Penicillium chrysogenum* is suppressed.[80] Concentrations of common salt up to 2% stimulate the production of penicillin by *Penicillium notatum*.[81] Sodium nitrate has been found a valuable source of nitrogen for the culture of this mould.[82-84] Although sodium nitrate was not found to inhibit the growth of the aerobic pathogens *Clostridium botulinum, Cl. lentoputrescens* and *Cl. sporogenes*,[85] the salt is widely used in conjunction with sodium chloride for curing meat.[86-90] The nitrate is partly reduced to nitrite which forms a good red colour with haemoglobin and partly to hydroxylamine which inactivates catalase, the resulting hydrogen peroxide killing *Clostridium*. Sodium nitrate appears to suppress the growth of *Azotobacter* cultured from soil.[91] *Actinomycetaceae* will tolerate much higher concentrations of sodium sulphate than of sodium chloride[92] whereas *Paramoecium* is rapidly killed by low concentrations of the sulphate.[93]

(iii) Bactericidal Action

Sodium chloride is bactericidal at high concentrations to many, though not all, organisms[94,95] and when injected into human beings so as to raise the blood content by as little as 0•01% the bactericidal power of the blood is greatly increased.[96] It does not affect the germicidal action of disinfectants of the hydroxyquinoline or organic mercurial type.[97]

Sodium hydroxide is a powerful bactericide[98] which however has little action on spores at room temperature.[99] The time T required to kill 99•9% of organisms at a soda concentration C and temperature t°C., is expressed by the equation:-[100-101]

$$\log T = 4{\cdot}9815 - 1{\cdot}7912 \log C - 0{\cdot}05630\ t$$

The velocity constant of the rate of disinfection has been determined[102] and other logarithmic equations have been proposed.[103] The mortality rate is highest during the first five minutes of treatment.[104] The bactericidal efficiency is correlated with the pH of the solution, falling off abruptly as the pH falls below 10.[103-106] The addition of other sodium salts, such as the chloride, carbonate or phosphate, markedly reduces the time required to kill 99•9% of organisms without affecting the pH,[105,107-111] and it has been suggested that the effective agent which penetrates the cell is undissociated sodium hydroxide. At the same normality the sterilizing order is (1) caustic soda (2) trisodium phosphate (3) sodium carbonate, but at the same pH the order is reversed, (1) sodium carbonate (2) trisodium phosphate (3) caustic soda.[109] The bactericidal action of dog saliva is due to the presence of sodium carbonate.[112] Sodium bicarbonate at a concentration of 3% is effective in preventing the germination of spores of the moulds *Penicillium italicum* and *P. digitatum* on citrus fruits. This action is independent of pH and is specific for the sodium ion.[113] Sodium iodide, on the contrary, is much less effective than potassium iodide against *Escherichia coli* and *Staphylococcus aureus* at neutral pH.[114] Addition of trisodium phosphate to pathological specimens is found to remove contaminant micro-organisms in the cultural diagnosis of tuberculosis.[115]

A number of bacteriophages are rapidly inactivated by solutions of sodium salts, sometimes in concentrations as low as 0•1M.[116-119] Calcium is antagonistic to this action and it is suggested that the inactivation may be due to replacement of calcium ions in the phage.[120] The kinetics of inactivation have been studied, the reaction constant exceeding 10^6.[121] Sodium chloride appears to affect the adsorption of phage on to the host cell but the effect is variable.[122] The rate of production of *Staphylococcus aureus* phage is however increased 5-10 times by the presence of 0•25M.-sodium chloride.[123] Sodium pyrophosphate increases the resistance of a phage to ultra-violet light, this action being inhibited by sodium chloride.[124]

(iv) Metabolic Effects

The oxygen uptake by many bacteria, both halophilic and halophobic, is increased by low concentrations of sodium chloride and decreased by high concentrations.[125-129] Although many other salts can be substituted for sodium salts, in some species the sodium cation is more stimulatory than the chloride ion.[127-128] Sodium appears to be necessary for the metabolism of *Lactobacillus arabinosus*[130] but not for that of *Escherichia coli*,[131] while sodium phosphate could not be substituted for potassium phosphate as a growth factor for *Micrococcus pyogenes*.[132] Glycolysis by resting cells of *Lactobacillus arabinosus* is inhibited by sodium ion when potassium is deficient,[133] whereas fermentation by *Saccharomyces cerevisiae* is stimulated. The lag phase of fermentation by this yeast is progressively lengthened by increasing salt concentrations but the effect of salt may be more directly on cell division than on metabolism since the nitrogen content of the yeast increases.[134] An increase in extractable amino acids is found in other yeasts adapted to salt-rich media.[135] Assimilation of amino acids by certain bacteria and yeasts is found to be accompanied by changes in the balance of sodium and potassium inside the cells.[136] A strain of *Proteus* also requires both sodium and potassium for the deamination of aspartic acid.[137] An insufficiency of sodium ions in the medium prevents the production by yeast of a water-soluble vitamin believed to be of the B group.[138] Sodium chloride weakens the activity of the endogenous amylase of *Aspergillus oryzae* but strengthens that of the exogeneous amylase.[139] Both the adenosinetriphosphatase and inosinetriphosphatase activities of the virus causing avian erythromyeloblastic leukosis are stimulated by sodium chloride.[140] The salt also stimulates the production of lycopene at the expense of β-carotene by *Neurospora sitophila.*[141] Several studies have been made of the metabolism of carbon assimilated from sodium ^{14}C-bicarbonate.[142-146]

(v) Morphological Effects

Morphological changes are found in many species of bacteria after treatment with sodium chloride.[148-150] For *Vibrio comma,* pH is an additional factor and sodium chloride widens the range of pH tolerance.[151] In some bacteria and algae the changes are first, swelling followed by formation of chains of cells and finally, production of long filaments by elimination of the transverse cell walls.[152-154] The swelling caused by a series of different cations follows the Hofmeister series and thus may not be a specific effect.[153] In *Photobacterium phosphoreum* distinct changes in the appearance and arrangement of chromatin can be observed in the nucleus after exposing the cells to different concentrations of sodium chloride.[155]

(vi) Effects on the Permeability of the Cell Wall

Attempts have been made to explain the action of sodium ions on micro-organisms as a direct effect on the permeability of the cell wall,[156,157] but it is probable that the true explanation is more complex.[47] Evidence from direct analysis with yeasts,[158] electrophoretic measurements with *Micrococcus halodenitrificans*[24] and radiotracer studies with *Escherichia coli*[159] indicate that the cell wall of these three species is freely permeable to sodium ions, but *Aerobacter lactis* was found to assimilate rubidium only when exposed to a mixture of sodium and rubidium ions.[160] Low concentrations of sodium chloride increase the outward diffusion of ammonia from cells of *Escherichia coli.*[16]

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Effects on Plant Growth

(i) Occurrence in Soils

Saline soils often occur near the sea where rainfall is low,[1,2] but may arise in regions where percolating ground waters have become enriched with salts.[3,4] Sodium carbonate and sodium sulphate may be formed by reaction of sodium chloride with the soil complex.[5,6] Water containing more than 2·5 millieqivs./l. of sodium carbonate is unsuitable for irrigation[7-9] owing to the resulting accumulation of sodium in the soil. Shrubs and vegetation in semi-arid regions may also cause accumulation of salt in soils.[10,11,131] Fumigation of soil has been found to cause increases in the sodium content.[12] Methods have been developed for determining the exchangeable and total sodium content of soils[13,14] and data have been published for some soils.[15]

The initial effect of sodium salts on soil is to deflocculate the clay complex thus increasing slightly the water percolation rate, but as sodium ion replaces calcium and other ions the soil swells, becoming transformed to a sticky mass, and the percolation rate falls off very drastically while the soil pH also rises markedly.[16-20] Sodium produces a greater depression of water permeability than any other ion and sodium salts have in fact been added to ponds and canals to prevent losses of water by percolation.[21,22] Almost complete loss of structure may be observed as a result of saturation with sodium and the soil loses its power of raising water by capillary forces.[23-28] Replacement of as little as 15% of the cation-exchange capacity of soils may destroy the structure and permeability.[29] The cohesion of the soil after drying is reduced by sodium[30] while the soils become very corrosive at certain water contents.[30-32]

Part of the sodium ions in soil appear to be present in a non-exchangeable form which may be steadily released as exchangeable sodium to offset losses through leaching.[33] The concentration gradient near soil particles is considerably greater in sodium- than in calcium-saturated soils[34] and calculations have been made of the concentrations of sodium and calcium ions in the Gouy and Stern layers round the soil colloid particles.[28] A linear relationship exists between free sodium ion concentration and pH in soil[35-37] but pH alone is not a good index of the degree of salinity of a soil.[38] Thus the pH of a sodium-saturated soil is higher in the presence of calcium carbonate.[39] Sodium ions may be removed from soil by electrodialysis, the rate depending on the degree of saturation and on the pH.[40] The percentage of free sodium ion also decreases with increasing moisture content of the soil.[41] The cation exchanges in soil for the systems sodium-calcium, calcium–sodium+magnesium etc. obey the law of mass action, are perfectly reversible and take place under conditions of strict equivalence.[42] It is not surprising therefore that treatment of soils with sodium does not invariably increase the availability of calcium[43] or of potassium[44,45] as has been thought. Sodium does however seem to modify the permeability of plant cell walls, as will be discussed later. Liming increases the exchangeable sodium of soil[46] by displacing it from the soil colloid, while sodium has been found to increase the availability of phosphate in soils.[47] Treatment of soils with sodium hydroxide or carbonate increases the soluble organic matter which absorbs iron and aluminium sesquioxides.[48] Sodium saturated soils absorb about the same amount of ammonium ion as calcium saturated soils[49] though the times required to reach equilibrium may differ.[50]

The reclamation of sodium-saturated sandy soils is most simply carried out by permitting rain to leach the salts from the soil. Thus rainfall during one winter reduced the sodium salts in a sandy soil reclaimed from the sea to 20% of the initial value at 25cm. depth and to 50% at 50cm. depth.[51] Clay soils are a more difficult problem owing to the poor drainage but good results have been obtained by adding powdered gypsum[52,53] or calcined lime.[54,55] As soon as the concentration of soluble salts has been reduced below about 7·5g. per l. in the ground water, crops may be planted, first sugar beet, followed the next season by cereals.[56,57] Cultivation should be avoided since this tends to destroy natural drainage channels.[58,59]

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(ii) Sodium Salts as Fertilizers

(a) Sodium Chloride

Sodium chloride was advocated as a fertilizer as long ago as the middle of the last century.[60,61] At normal levels of treatment the exchangeable sodium in the soil may be trebled and even quadrupled over a number of years.[62] Although sodium sulphate and sodium carbonate stimulate nitrification in the soil, sodium chloride supresses it probably because of its inhibiting action on *Azotobacter*,[63-66] and estimation of viability of this organism has been proposed as a method of rapidly assessing the salt content of soils.[67] Sodium ions have an unfavourable effect on formation of humus from straw.[68]

Sodium chloride cannot be substituted completely for potash but can replace a considerable fraction of the potash applied as fertilizer,[69] although this replacement is not equivalent, some 2-3 times as much sodium as potassium being required to produce the same yield. Crops requiring large amounts of potassium respond better to treatment with sodium than crops requiring little potassium. The anion as well as the cation affects the response of crops. Thus the yield of crops sensitive to chloride ion, such as potatoes, may actually be decreased by treatment,[70] whereas the yield of chloride-insensitive crops is considerably increased. The beneficial effects of sodium salts are regarded as due partly to a favourable effect on the water balance and partly to replacement of potassium. Thus sodium applied to the soil migrates almost entirely to the leaves of sugar beet, reducing their requirement of potassium so that a larger proportion of this latter element is available for the root.[71] Sugar beet does in fact show a very marked response to fertilization with sodium chloride, the yield of both leaves and roots being appreciably increased. In many cases the actual sucrose content of the roots increases[72-77] but this is not always so[78-81] and it is possible that this factor is dependent on the ratio of sodium and potassium available to the plant. Other crops that benefit from sodium chloride fertilization are table beets, celery, Swiss chard, mangels,[78] asparagus,[82] alfalfa,[83] rutabagas, carrots,[84] oats,[85-87] flax,[86] ladino clover, sudan grass,[87] meadow and rye grass,[88] vetch[91] and cotton,[89-91] though cotton appears to be very sensitive to the sodium-potassium ratio and the yield may be depressed by applying too much sodium salt.[90-93]

(b) Sodium Nitrate

Sodium nitrate is widely used as a source of nitrogen for crops. The sodium ion tends to increase the pH of the soil and increases the availability of other cations by displacing them from the soil colloid complex. It may also have a favourable effect on the permeability of the soil. When used on suitable soil the salt may show a marked superiority over other nitrogenous fertilizers.[94] The commercial source of sodium nitrate is Chile nitrate and the favourable effects of the minor trace elements in this salt have been extensively reviewed,[95] the most important being boron.[96,97]

The increase in pH of the soil caused by repeated treatments with sodium nitrate depends on the buffering capacity of the soil[98,99] and the difference in pH between soils treated with sodium nitrate and with ammonium sulphate over a period of 11 years ranged from 0•3[100] to 2•3 units[101] depending on the soil type. There is a marked increase in the amounts of available calcium,[102,103] potassium[104] and phosphate.[103-106] The rainfall required to leach sodium nitrate almost completely from the surface 5cm. was 160mm. for a sandy soil and 275mm. for a loam, the corresponding figures for ammonium sulphate being 200mm. and 225mm.[107] This effect may be partly attributed to changes in water permeability.[108] Sodium nitrate stimulates nitrification in the soil[109] and gives higher recoveries of nitrogen than ammonium sulphate.[110-111] Comparative trials with different fertilizers show a marked superiority of sodium nitrate for sugar beet,[112-114] potatoes,[115] cotton[116,117] and annual bluegrass[118] but inferior results with sugar cane,[119] tea[120] and Austrian winter peas.[121] There is no advantage in the case of apple trees[122] where the sodium nitrate appeared to favour the incidence of cork disease.[123]

(iii) Occurrence and Distribution in Plants

A method has been developed for the estimation of the amount of sodium in plant tissues based on precipitation of sodium magnesium uranyl acetate.[124] Early literature on the occurrence of sodium in plants has been reviewed.[126,127] It is difficult to quote definite figures since the sodium content varies widely depending on the amount of available sodium in the soil, on the particular plant organ examined, on the age of the plant and on the season.

Surveys have been made of the sodium contents of halophytes growing in saline soils near the sea.[128-130] The anion associated with sodium in the ash of halophytes has been found to vary with the total ash content; thus chloride and carbonate prevail in an ash content of 5-10%, sulphate in 15-20% ash and chlorides in ash contents greater than 20%.[131] Determinations of the sodium content of many hundreds of species of plants have been made by chemical and spectrographic methods.[124,132-135] The extreme values range from 0·0017% in the fruit of *Aesculus Hippocastanum* to 3·5% in *Zostera marina*. Periodic determinations over different lengths of time have been made with vines,[136] tea,[137] *Artemesia*,[138] legumes,[139,140] cotton,[141] grasses and cereals[142-144] and oranges.[145] Not only does the sodium content generally increase with the age of a plant[146] but there is also a tendency for it to rise from a low value in spring to a maximum in autumn and then to decrease gradually during the winter months.[147-150] The sodium content in some species appears to vary inversely with the nitrogen, phosphorus and potassium contents.[148-150] The ratio of potassium to sodium content also shows great variation with species, extreme values of K/Na being 1040 in *Sambucus nigra* and 3·06 in *Malva rotundifolia*,[151] and in addition with the age of the plant tissue or organ, with the season[152] and with the conditions of fertilization.[153-155] Sodium accumulated in the leaves of sugar beet (7·8% dry weight) and not in the root (0·8%)[156] while different leaf groups had differing contents.[157] Sodium was highest also in the leaves of the sugar cane and there was some evidence of migration from dying leaves to the living ones.[158] In the rubber tree,[159] and orange tree,[160] however, sodium was negligible in the leaves, being concentrated in the twigs and small roots. The roots of English boxwood infested with nematodes contained higher levels of sodium than did healthy plants.[161]

(iv) Requirements of Sodium by Plants

Although methods exist for culturing plants in an environment free from sodium,[162] it has proved very difficult to demonstrate a definite requirement for sodium.[163] Symptoms of sodium deficiency have been described[164-166] somewhat resembling those of potassium deficiency, and there is considerable evidence that sodium acts by replacing potassium to some extent although it cannot do so entirely.[167-169] The theory has been advanced that sodium has a growth-stimulating action independent of potassium[170,171] and it is suggested that it plays a role as an enzyme-activator.[172]

(v) Tolerance of Plants for Sodium

Apart from assessment of crop yields, many techniques have been devised for studying the tolerance of plants to sodium, including growth in sand cultures,[173] elongation of seedlings,[174] and measurements of starch synthesis in leaves,[175] of plasmolysis[176] and of yellowing of leaves.[177]

The tolerance of plants is affected by many factors, one of the most important of which is the phenomenon of adaptation.[178-181] Thus pre-treatment of seeds with hypertonic solutions of sodium chloride enables the plant to tolerate a higher degree of salinity than normal, while salt-resistant ecotypes are often found growing in saline soils.[182] The moisture tension of the soil has an effect on the resistance to salt[183] and attempts have been made to interpret tolerance in terms of the osmotic pressure of the soil solution[184,185] and of the electrical conductivity of this solution.[186,187] Certain roots differ in their readiness to penetrate into saline layers of soil and also show differences in their ability to withdraw water from adjacent non-saline layers.[188] Tolerance to salt may be due to the ability of the plant to accumulate sodium ions without deleterious effects,[187] the critical concentration being perhaps that required to kill or inactivate the enzymes in the roots which are responsible for growth.[178] Calcium ions[178] and trace elements[189] have been found to increase this tolerance but an excess of exchangeable cations may enhance the toxic effects.[190] Presumably the correct ionic balance is important and there are marked variations in the response of plants to the replacement by sodium of different percentages of the total exchange capacity of the soil. Thus avocado is injured by replacement of 4-7% of the exchangeable bases by sodium whereas tomato can tolerate replacement of 60-70%.[191-195] A reduction of temperature improves the tolerance of many plants to salt.[196] The germination of seeds is more sensitive to sodium salts than are the corresponding seedlings, and chlorides are more toxic to seeds than sulphates.[197-201] The sensitivity of rice and maize plants also decreases markedly with age.[202-204]

Typical halophytes found in salt meadows are *Glaux maritima*, *Aster trifolium*, *Erythraea pulchella*[205] and *Nitraria schoberi*, the latter being able to tolerate up to 8% of sodium chloride.[206] A number of grasses including *Agropyron repens* are able to tolerate 1·5-2·0% of salt.[207] Rye grasses, Arabian alfalfa, fescue,[207] cabbage[208] and *Astragalus*[209] will tolerate 1·0-1·5%, Wimmera rye grass,[210] millet[207] and spring wheat[207] tolerate 0·6-1·0% while tomatoes,[208] cotton,[211,212] wheat[213] and green beans[214] tolerate 0·3-0·6% of salt. Guayule[215] grows in concentration not exceeding 0·3% while tobacco[216] is very sensitive, failing in salt concentrations greater than 0·01%. Irrigation water should not contain more than 0·10-0·15% of salt for tomatoes,[217] sugar beet[218] or rice.[219] Concentrations of salt in culture solutions of 0·05-0·10% may depress the growth of young plants of wheat, barley and peas although under certain conditions 0·4% has proved stimulating.[220] Pangola grass has a high requirement for potassium, two thirds of which can be substituted by sodium.[221] Barley and wheat are killed by an increase of 0·2-0·3% in the concentration of sodium chloride in soil but the toxicity of sodium sulphate only becomes acute at concentrations exceeding 1·5%.[222,223] Application of about 10lbs. per tree of sodium chloride kills maple, birch, or oak trees[224] and the salt is 5-10 times as toxic to trees as calcium chloride.[225] Sodium chloride is believed to be a factor in the collapse and leaf fall of citrus trees since affected trees are found to have high sodium contents.[226,227] Sodium chloride is more toxic than sodium sulphate and sodium carbonate least toxic to seedlings of pine, larch, aspen, birch and maple.[228] Sodium carbonate is, however, very toxic to many species.[173,174,188,229]

Sodium salts have been used as weed killers and selective fungicides against pathogenic fungi. Thus sodium chloride proved an effective herbicide, killing many weeds in stands of sugar beet[230,231] but was not generally successful in other applications, since it often caused stimulation of weeds after an initial reduction.[232,233] The salt was found effective, sometimes in conjunction with other agents, for the control of cereal rusts,[234-236] *Phylloxera* in vines,[237] clubroot of cabbage[238] and both root-rot[239] and yellow disease[240] of sugar beet but less effective against *Fusarium* wilt of tomato.[241] A related fungus, *Fusarium oxysporum cubense*, was inactivated by the application of sodium nitrate[242] which also killed the ascospores of *Venturia inaequalis*, but

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unfortunately at dosage levels harmful to the crop.[243] Sodium nitrate is also effective in controlling onion smut.[238] Trisodium phosphate effectively inactivates potato virus X but the utility of this finding in agriculture is doubtful.[240]

(vi) Physiological Effects of Sodium

(*a*) General Effects

There have been many observations of physiological disturbances in plants which have been attributed to sodium ions but these observations are so disconnected that it is difficult to integrate them into a general scheme. A number of general reviews and discussions have been published.[244-250]

In plants many growth responses to sodium chloride can be attributed to a physiological scarcity of water.[251] Thus in tomatoes there is a reduction in height and diameter of stems, thickening of the walls in xylem tissue and a reduction in cambium activity, all of which may be caused by a higher osmotic pressure in the cells and tissues.[252] At lower concentrations of salt the effects may be due to changes in the physical properties of the soil and to a reduction in the amount of available calcium.[253] In the true halophytes such as *Salicornia herbacea*, sodium chloride causes an increase in the degree of succulence, an effect which is specific for the chloride ion. There is also a specific effect on transpiration.[254,324] In saline soils there is an increase in the concentration of the cell sap of this species[255] and also of *Atriplex verruciflera* and of wheat[256] while the water requirement of the last two species is greatly reduced. Sodium chloride decreases transpiration and also the silicic acid content of the leaves[257] but increases leaf growth[258,259] and oxalic acid formation.[260-263] The formation of carotene is also supressed by sodium in sugar beet and other plants.[264] Although the amount of starch present in the leaves of bean plants is reduced in saline soils,[265] sodium appears to reduce the amount of starch metabolised per unit of cellulose formed in barley seeds[266] but increases the sugar content of timothy.[267] Sodium chloride is responsible for the development of tirak (a magnesium deficiency disease) in cotton[268] with resultant disturbances in protein synthesis. The salt inhibits curvature of the coleoptile of *Avena*[269] and reduces the transpiration coefficient of tomatoes.[270] Chlorophyll production is reduced in sorghum[271] and the percentage of nitrate in beans is increased.[272] Sodium nitrate increases the production of vitamin C in tomatoes[273] and of nicotine in tobacco.[274] Root tumours are produced by a treatment of plants with salts[275] containing sodium.[22] An attempt has been made to correlate the sodium content of vegetables with their food value.[276]

(*b*) Interaction Between Ions.

Considerable attention has been given to the effect of one ion on the uptake of other ions by plants and to the interaction between ions in plants. The picture is becoming clearer and certain general principles are beginning to emerge. The assimilation of ions from soil by plant roots appears to be related to the relative degree of saturation by both plant tissues and soil complex by the ions but there is little correlation with the actual amounts of ions in the soil.[277-279] Results are unfortunately not always clear cut, perhaps because of failure to recognise the essential unity of the plant-soil relationship. There is some evidence that different ions may have different effects on the permeability of the plant cell walls. Thus sodium chloride is found to increase the absorption of nitrogen and phosphate[280,281] but this may be due to increased availability of these substances in the soil.[282] In sugar beet sodium appears to accumulate until a constant level is attained irrespective of the concentration in the soil[257] and the uptake soon stops, the sodium being concentrated largely in the leaves.[283] In citrus plants however there is little accumulation in the leaves but the sodium content of the roots may be correlated with the concentration of sodium in the soil.[284] Cotton gives best growth when sodium represents only 3·5-4·1% of the exchangeable bases.[285] A typical halophyte continues to take up sodium until very high internal concentrations are reached.[286] In barley and wheat the ions are absorbed in equivalent amounts from sodium chloride at low concentrations, the cation being preferentially absorbed at higher concentrations.[287,288] In other species of plants the anion or cation may be predominantly taken up, the behaviour often differing with species and even with the variety.[289-291] Excess of chloride ion seems to be particularly toxic.

Sodium may increase the uptake of potassium, or may have no effect or even decrease the uptake, the actual effect often depending on the age of the plant, and on the particular part of the plant examined.[292-297] The absorption of sodium by sugar beet has also been found to depend on the level of potassium in the soil.[298-300] Although it has been argued that sodium cannot replace potassium in plants,[301-303] there is much evidence that sodium can be substituted for potassium at least to a limited degree.[304-313] Marked changes occur in the sodium-potassium ratio in sugar cane at different stages of development[314] while in peas the ratio varies with the sodium content.[315] The factors affecting the ratio of exchangeable sodium to potassium in sugar beet soils have been reviewed.[316]

An increase in the concentration of sodium salts in soil decreases the uptake of calcium.[257,317-323] This effect is partly due to differences in the availability of the ion but there may also be a specific effect of sodium on permeability since in the presence of calcium carbonate the uptake of both calcium and sodium increases with increasing sodium concentration.[324] Calcium deficiency in oats does not however increase the uptake of sodium.[325] Symptoms of magnesium deficiency may be induced in sugar beet by the application of sodium chloride although the magnesium content does not appear to be greatly affected.[326] In saline soils manganese and iron chlorosis may develop but this may be associated with an inability of the plant to transport these essential metals through the tissues rather than to a decrease in the rate of uptake.[327,328] The boron content of plants grown on saline soils appears to be normal.[329]

The stem epidermal cells of the halophyte *Suaeda maritima* have only low permeability to sodium chloride.[330] Sodium nitrate solutions increase the water permeability of the epidermis of *Allium cepa*[331] while sodium hydroxide has a similar effect on many seeds.[332,333] Oat roots simultaneously excrete and absorb both sodium and potassium whereas yeast, in the absence of glucose, excretes potassium and absorbs sodium.[334] The absorption of sodium by rye seedlings was found to be frequently less than the theoretical sorption calculated from transpiration measurements.[335] Maize shows selective absorption, being able to exclude sodium[336] but beet appears to be unable to distinguish between the two metals.[337] Sodium increases the absorption of rubidium[338] and does not compete with it.[339] The behaviour of the electrical potentials of plant roots in sodium chloride solutions is different from that in equivalent solutions of potassium chloride[340] and a definite potential exists at which the uptake of a specific ion is stimulated, sodium uptake being enhanced at −2·10V.[341] Potential measurements also suggest that sodium may be bound less strongly than potassium on alfalfa roots and more strongly on soyabean roots.[342] It has been suggested that the movement of ions into root cells may be explained by assuming the cytoplasm to consist of non-mobile anions.[343,344] An attempt has been made to explain the absorption of ions in terms of the electro-osmotic flow under the influence of the electric field in the cell wall membrane, the direction of movement of any ion species thus depending on its ionic mobility.[345,346] The Donnan equilibrium applies to the absorption of calcium and sodium by both barley and pea roots.[345] Sodium influences the movement of calcium inside the plant tissues,[346] but not that of potassium. Displacement of calcium may arise through the replacement by sodium in such salts as calcium pectate.[347] Radiotracer experiments show that sodium is rapidly transported through the plant tissues and can move in both directions.[348,349] The rate of movement of sodium is more rapid than that of potassium.[350] Measurements of the potential between the root protoplasm and the surrounding solution suggest that penetration of metallic ions may take place by replacement of hydrogen ions in the surface of the protoplasm.[351]

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Effects on Marine and Freshwater Organisms

(i) Requirements, Distribution and Tolerance

A definite nutritional requirement for sodium has been demonstrated for some marine bacteria,[1] *Myxophyceae* (blue-green algae),[2-4] planktonic algae[5] and *Ulva lactucca.*[6] Some species seem, however, indifferent to the presence or absence of sodium. In the absence of sodium eggs of the sea urchin, *Strongylocentrus purpuratus*, are not fertilized, while the spermatozoa are also immotile.[7] Determinations have been made of the sodium contents of many marine species including algae,[8-12] sponges,[13] gastropods,[14,15] bivalves,[16] echinoderms,[17-19] polyps[20] and fish.[21-23] Although, as might be expected, the content tends to be higher than in terrestial organisms, there is very great variation even in the same species. Thus the sodium content on a dry weight basis in the seaweed *Eisenia bicyclis* is 2·35–2·82 (very close to the content of sea water) while in *Sargassum fulvellum* the range is 1·10–4·05.[11] The sodium content of seven species of crustacea is 0·1–0·4% less than that of the water in which they live.[24] In many organs of the fish *Scorpaena porcus* the percentage of sodium varies with age, reaching a maximum at five years and then declining.[25] The ratio of the sodium chloride contents of vitreous humor and of plasma in the marine fish *Lophius piscatorius*, 0·82, is quite different from the ratio found in mammals.[26] The blood of this fish[27] contains 0·425% of sodium ion. The sodium content of the blood of the fresh water shell-fish *Anodonta*, varies with that of the surrounding water, being 0·033% in fresh water and 0·102% in diluted sea water with a sodium concentration of 0·107%.[28] The salt content of the sea urchin *Echinus esculentus* is higher in eggs with an intact fertilization membrane[29] while that of the roe of lake trout is 0·17%, lower than in marine species.[30]

The tolerance of fish to changes in salinity has been reviewed.[31,32] Many marine bacteria[33] and diatoms[34,35] are able to tolerate concentrations of salt of the order of 10% and even 25%. A 3% solution of sodium chloride is toxic to steelhead trout fry at 1-2 weeks of age but not to older fry.[36] The toxicity of sodium chloride has also been determined to molluscs,[37] to the marine worm *Arenicola*,[38] and to goldfish.[39] Solutions of potassium salts inhibit the toxicity

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of sodium chloride to many crustacea.[40,41] Sodium chloride is less toxic to *Leponis macrochirus* than are sodium nitrate or sodium sulphate.[42] A number of samples of supposedly pure sodium chloride have been found to contain an impurity, possibly a silver salt, which causes haemolysis of fish erythrocytes.[43,44] The problem of river pollution is serious and there have been a number of studies of the toxicities to fish of compounds occurring in factory wastes including sodium salts.[45-51] Sodium hydrogen sulphide and sodium sulphide are the most toxic, followed by sodium hydroxide, while sodium sulphate, a common constituent of wastes, is much less toxic.[49,50,52] There is evidence that the toxic threshold is lower for combinations of two or three salts than for individual salts.[53]

(ii) Permeability and Ionic Regulation

Many studies of the permeability of the cell walls of marine organisms have been carried out using radioactive sodium salts. The rate of penetration of sodium ions into *Spirogyra* and *Nitella* is very rapid, a concentration ten times that of the surrounding solution being reached in fifteen seconds. Ions appear to move equally freely in both directions[54] and the rate of uptake is exponential.[55] Penetration into *Valonia* is slower,[56] and the ion accumulates in the protoplasm and not in the cell wall or sap. *Halocystis*, on the contrary, accumulates sodium in the cell sap and not in the protoplasm.[57] Penetration of sodium ions into eels is accelerated by removing the slime coat.[58] The sodium content of the blood of eels is related to the protein content.[59] Sodium is actively taken up through the gills of fish against a concentration gradient,[60] the rate of exchange being equal to about 1% per hr. of the total amount of sodium present in the body.[61] The sodium content of the blood of crustacea changes with the salinity of the surrounding medium but not proportionately.[62,63] The sodium content of the blood of *Ligia oceana* is much higher than that of sea water and the animal can withstand considerable desiccation and hydration without ill effects. This behaviour is of course advantageous in a shore-dweller.[64] Sodium increases the permeability of sea urchin eggs to dyestuffs.[65] Many marine algae such as *Ulva lactuca* have a high potassium and a low sodium content, sodium being excluded by a metabolic mechanism. Penetration of sodium is increased by the enzyme inhibitor, iodoacetate, in the dark but not when the alga is exposed to light. There is some evidence that sodium is largely unionized when inside the alga.[66-69] The mobility of potassium ions in the outer protoplasm of *Nitella* has been calculated from potential measurements to be forty times that of sodium ions.[70] A number of fresh-water animals such as *Hydra* and *Potamobius* obtain their salts from the surrounding water and maintain a constant concentration in their tissues appreciably higher than that outside.[71-73]

(iii) Specific Biological Effects

The luminescence of some marine organisms depends on the concentration of sodium chloride;[74] in others it is independent of this concentration.[75] The basal metabolism and oxygen consumption of *Asterias rubens*[76,77] and of salmon fry[78] also depends on the concentration of sodium chloride, as does the critical temperature of heat narcosis in crabs.[79] Antagonism between sodium and other ions has been studied in a number of species of crustacea and protozoa which show different responses of locomotion, cardiac activity and motility in different ionic environments.[80-82]

Sodium chloride weakens and disrupts the surface membrane of *Amoeba proteus*, causes the protoplasm to become more fluid and increases the rate of division.[83-88] Similar effects are caused in the protoplasm of *Actinosphaerium* and *Spirostomum*.[89] The toxicity of sodium chloride to many protozoa is probably due to similar action on the protoplasm.[90,91] From reproduction studies on *Chilomonas*, sodium and potassium appear to have additive effects, antagonism being found between sodium and calcium.[92] Much stronger positive chemotropism is however shown by *Paramecium* to sodium than to potassium salts.[93]

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Effects on Invertebrates

(i) Insects

From a study of the sodium and potassium contents of a number of species of insects it is concluded that insects with a high sodium content have a more

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ancient origin while those with low sodium and high potassium contents appeared later in the Tertiary period, in parallel development with phanerogamic plants.[1] Certainly most phytophagous insects have very low blood-sodium contents, e.g. *Popillia japonica*[2] 0·0465%, *Samia walkeri*[3] 0·0597%, *Bombyx mori*,[4,5] 0·0332%, while the *Bombyx* pupa contains less than 0·0003%, whereas the larval haemolymph of the blood sucking horse bot fly, *Gasterophilus intestinalis*, contains[6] 0·474%. No significant differences are found in the sodium contents of the mosquitoes *Culex tarsalis* and *Culex stigmatosoma*.[7]

The viability of *Drosophila* is not affected when the flies are deprived of 95% of their sodium.[8] Many mosquito larvae develop in pools of saline water and some species are able to tolerate quite high concentrations of sodium chloride.[9-12] There is often an optimum concentration for development which varies with the species. Thus *Aedes zammitti*[13] requires an optimum concentration of 20–30%, *A. caspius* 1–5% and *A. aegypti* 0·5–1%.

The movement of sodium in insects has been studied by means of radioactive tracers. Exchange between the external medium and the insect body takes place mainly through the anal papillae, though some enters through the body wall,[14,15] the time for half exchange being about 62hr. The permeability of the cuticle of *Sialis lutaria* larvae to sodium and chloride ions[16] is $1{\cdot}04 \times 10^{-4}$cm.hr.$^{-1}$ at 17°C. The sodium content of the haemolymph of many species is maintained constant probably by the process of resorption of a portion of that excreted in the urine.[17-20]

Sodium chloride stimulates the chemoreceptors of a number of species of insect,[21-23] the threshold for the bee being 0·24M. as against 0·009M. for man. A number of insect enzymes are inhibited by high concentrations of sodium chloride but it is probable that this is a salt effect and not specific.[24-26] The optimum ratio of sodium to potassium ions for maintaining the normal heart beat varies with the species but sodium is usually not very toxic and its concentration can often be raised with little apparent effect.[27,28] The development of *Drosophila* and *Bruchus* is not greatly affected by high concentrations of sodium.[29,30] Good kills of the elegant grasshopper, *Zonocerus elegans*[31] and of pinebark beetle[32] have been obtained by spraying strong solutions of common salt, the salt being more effective than arsenic against the beetle.

(ii) Helminths

The salt concentration of the body fluid of the helminth *Ascaris lumbricoides* is also maintained constant by active transport even when the concentration of the surrounding medium is varied.[33] Sodium chloride weakens the photic orientation of the earthworm, *Allolobophora foetida*. The effect of other ions in combination with sodium chloride has also been studied.[34-36]

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Sodium and Mammals

(i) Growth Requirements

An adequate supply of sodium chloride in the diet is essential for the continued health of mammals particularly during the period of active growth. Young rats, dogs, pigs and cattle make very poor growth when deprived of salt.[1-11] The minimum requirement appears to be about 0·05% of the diet,[2,3] but the actual figure may be related to the composition of the diet.[6] Milk production of cows is appreciably increased by the addition of salt to the rations.[11] The optimum requirement of the chicken is about 1%, and at lower levels growth, health and egg production suffer.[12-16] The nitrogen retention of laying hens is greatly reduced on a restricted salt diet.[17]

A normal man requires between 1 and 2g. of sodium chloride per day.[18] A diet restricted in salt may cause loss of weight in infants[19] while continued restriction may cause sodium deficiency resulting in low sodium levels in the blood plasma.[20] The requirement of sodium during normal growth in man is found to follow the equation:-[21]

$$\text{Na (meq./kg.)} = 290W^{-0\cdot168}$$

where W is the body weight. In some diseases it is desirable deliberately to restrict the intake of sodium and a number of sodium-free diets have been devised.[21,23] Drinking water may provide substantial amounts of sodium to persons on such diets and the water supply must be carefully considered in such cases.[24] Table salt substitutes with low sodium contents have also been developed.[25,26] Increased doses of common salt have been found beneficial in the treatment of sprue[27] and Addison's disease.[28]

(ii) Toxicity

Sodium chloride is not normally regarded as a poison but too low or too high an intake can upset the mineral balance of the body and can cause demon-

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strable changes in certain organs.[29] In some diseases the salt intake must be carefully regulated to avoid undesirable effects.[30] Rats are able to tolerate large intakes of salt provided they are allowed sufficient water[31] but salt appears to be toxic if potassium deficiency is present.[32,33] The lethal dose of physiological saline (0·9%) injected intravenously into mice is 6·9ml. per 20g.[34] Chickens are more sensitive, the lethal dose of common salt being 4g. per kg.[35,36] The symptoms of excessive salt intake in fowls are loss of weight and feathers, diarrhoea and weakness[37] while oedema and ascites may be produced.[38] Severe symptoms have also been observed in cows,[39,40] sheep[41,42] and pigs[43] allowed to ingest excessive amounts of salt, a percentage of the herds either dying or having to be slaughtered. Excess sodium chloride produces haemorrhages in the heart, severe bloody congestion in the kidneys[33,36] and hyperaemia in the brain.[44] Excessive excretion of sodium chloride through the skin of cattle may give rise to intense itching and there may be destruction of the red blood cells with haemoglobinuria.[39]

Bromide intoxication is more severe in persons on a low salt diet and sodium chloride is a specific antidote.[45,46] Administration of sodium chloride has also proved beneficial in cases of poisoning by phosgene[47] and iodoacetate.[48] The lethal dose of sodium hydroxide for man is less than 10g.[49] and the pathological effects and symptoms produced in animals have been described.[50-52] The maximum concentration of caustic soda tolerated by the skin is 1%.[53] The median lethal dose of sodium dihydrogen phosphate for rabbits is 1·48g. per kg.[54] Radioactive sodium is now commonly used for studying the metabolism of the element in the body and doses equivalent to 53 millicuries have been given to human beings with no observable clinical results;[55] the median lethal dose for mice is 30 microcuries per g.[56]

(iii) Distribution of Sodium in Mammals

Methods for the estimation of sodium in biological fluids have been reviewed.[57] There are several chemical methods,[58-60] including colorimetric and iodometric methods, but there is increasing use of the flame photometer[61,62] and conductivity methods.[63] Measurement of the potential between a solution and a sodium-mercury electrode has been used to determine the activity of sodium in blood serum and hence the amount of sodium bound by the proteins.[64] The activity in serum is the same as in a pure solution of sodium chloride.

The technique of using radioactive sodium in biological experiments has been described.[65-67] The method has been used chiefly for determining the volume throughout which sodium chloride is distributed after introduction into the body[68-70] or the rate of redistribution in healthy[71,72] and diseased subjects.[73-75]

The distribution of sodium in various tissues and organs of animals is given in Table II.

In rats, rabbits, cats and pigs there is more sodium than potassium in the body at birth but the content of sodium falls steadily and that of potassium rises until at maturity there is twice as much potassium as sodium.[106] Sodium exists in bone in a stable form which is not removed until the tissue is resorbed.[107] About 87% of ingested radioactive sodium taken up by the teeth of dogs was found to be associated with the organic part of the tooth.[108] Both sodium and carbonate contents of bone increase with the age of the animal.[109] The ratio between the concentrations of sodium in the aqueous humor and the blood serum is relatively constant in different species, ranging from 1·03,[110] 1·042 in the cat to 1·07 in the pig.[111] These ratios are usually smaller than in the theoretical Donnan ratio, 1·12 for dogs. The turnover rate in the aqueous humor is 62·5min.[112] The sodium content of the eye lens increases when cataracts are formed by treatment with thyroxine.[113] Only 69% of the sodium

Refs. p. 1434

TABLE II.- DISTRIBUTION OF SODIUM IN ANIMAL TISSUES

Tissue	Species	Sodium %	Ref.
Intracellular	Dog	0·0805	76
Bone	Rat	0·349	77
Bone	Dog	0·527	110
Muscle	Rabbit	0·0851–0·0989	78
Muscle (red)	Rabbit	0·038	79
Muscle (white)	Rabbit	0·0584	79
Muscle	Guinea pig	0·0472	79
Muscle	Rat	0·0502	79
Brain (grey matter)	Rabbit	0·1319	80
Brain (white matter)	Rabbit	0·1217	80
Eye, lens	Rabbit	0·587	81
Eye, aqueous humor	Rabbit	0·092	82
Liver mitochondria	Rat	0·299–1·08 mean 0·69	83
Blood (whole)	Dromedary	0·231	84
Blood (whole)	Electric eel	0·392	85
Blood (whole)	Horse	0·219	86
Blood plasma	Dog	0·336	87
Blood plasma	Elephant seal	0·326	88
Blood plasma	Rabbit	0·331	78
Blood plasma	Rabbit	0·337	79
Blood plasma	Rat	0·313	79
Blood plasma	Guinea pig	0·317	79
Blood plasma	Horse	0·334	86
Blood plasma	Sheep	0·334	89
Blood serum	Dog	0·337	90
Blood serum	Rabbit	0·326	91
Blood serum	Rabbit	0·365	92
Blood serum	Cow	0·430	93
Blood serum	Cow	0·326	94
Blood serum	Goat	0·431	95
Blood serum	Horse	0·591 (NaCl)	96
Blood serum	Viper	0·390	97
Blood erythrocytes	Sheep	0·0782–0·269	98
Blood erythrocytes	Sheep	0·0782–0·180	99
Blood erythrocytes	Sheep	0·0671	89
Blood erythrocytes	Elephant seal	0·218	88
Lymph	Rabbit	0·310	91
Lymph (leg)	Rabbit	0·356	92
Lymph (intestine)	Rabbit	0·338	92
Lymph (liver)	Rabbit	0·370	92
Milk	Cow	0·296	100
Milk	Cow	0·050	101
Milk	Sheep	0·398	100
Milk	Goat	0·256	100
Milk	Mare	0·006	101
Gastric juice (fasting)	Dog	0·217	102
Gastric juice (after meal)	Dog	0·031	102
Intestinal juice	Dog	0·266	102
Pancreatic juice	Dog	0·300	102

continued on following page

TABLE II continued

Tissue	Species	Sodium %	Ref.
Bile	Dog	0•302	102
Semen	Bull	0•258	103
Semen	Boar	0•069	104
Cerebrospinal fluid	Dog	0•337	90
Cerebrospinal fluid	Dog	0•736 (NaCl)	105
Cerebrospinal fluid	Horse	0•591 (NaCl)	96

present in the bovine lens is ultrafilterable under pressure.[114] In 27 species of wild animals[115] the sodium content of the blood serum ranged between 0•336 and 0•424%, of whole blood between 0•261 and 0•405% and of erythrocytes between 0•032 and 0•137%. The content of human, horse, pig and rabbit erythrocytes varied[116] between 0•021 and 0•069. There is a close relation between the sodium and chloride ion contents of the blood of cows and it is not possible to reduce the concentration of one ion by feeding the other in excess.[117] Rabbits, hedgehogs, pigeons and sparrows exhibit a seasonal variation in the sodium content of the erythrocytes.[118] The sodium content of rabbit blood serum is changed by the administration of hormones such as testosterone or folliculin, an increase or decrease being produced depending on the dose level.[119] The sodium content of cow's milk may vary over a range of 140% independently of the salt intake.[120] The content is lower than that of the blood at the beginning of lactation but later tends to rise to the same value.[121] There appears to be an inverse relation with the lactose content.[122] The sodium and chloride ion contents of cow's milk are not equivalent and are related by a simple equation:-[123]

$$\%\mathrm{Cl} \doteq 1{\cdot}24 \times \%\mathrm{Na} + 18{\cdot}09$$

The chloride ion content is not affected by the ingestion of moderate amounts of sodium chloride but is increased by large amounts.[124] Both the sodium content and the sodium-potassium ratio of the blood have a positive effect on milk yield.[125] Sodium is the most abundant ion in the bile of vertebrates,[125,126] being 12–23 times the concentration existing in the liver.[128] There is a large increase of sodium in the brain and heart of guinea pigs maintained at an atmospheric pressure corresponding to a height of 6000m.[129]

The distribution of sodium in normal human tissues is given in Table III.

The most striking feature about the results in Table III is the wide range of values for any tissue found in normal individuals. This is perhaps not surprising since sodium in body tissues is in dynamic equilibrium with other anions and cations and moreover the actual content found at any instant will depend on the recent history of the tissue.

There is a decline in the sodium contents of all tissues from infancy to maturity, especially in the brain where the sodium content may fall to a half that at birth.[180] Changes in the sodium content of the human foetus from the 4th month to birth have also been described.[181] Sodium can be removed from skin by electrodialysis[182,183] but only 40–45% of the sodium present in bone is exchangeable with radioactive sodium[184,134] and it is suggested that the sodium forms part of an apatite complex.[185,186] The sodium occurring in blood serum is completely removed by electrodialysis[187,188] and less than 1% is precipitated with proteins by ethanol.[189] Both sodium and chloride contents show seasonal variations, decreasing in summer and increasing in winter.[190] The sodium content of the serum increases when common salt is ingested without food but there is little change when food is also ingested.[191,192] After injection of sodium chloride solution, the chloride ion is distributed very rapidly between blood and the tissues, about 8% remaining in the blood.[193] The actual ratio of the two ions is, however, subject to wide variations.[194]

TABLE III.- DISTRIBUTION OF SODIUM IN HUMAN TISSUES

Tissue	Sodium %	Method	Ref.
Whole body	0·212–0·270	Chemical analysis	130
Whole body	0·0957±0·0035	Radiotracers	131
Intracellular	0·0975±0·0046 (of intracellular water)		132
Intracellular	0·085 (of intracellular water)		133
Intracellular	0·082 (of body weight)		133
Bone	0·538		134
Skin	0·00122		135
Skin	0·0805±0·0023	Electrodialysis	182
Liver	0·121–0·255	Chemical analysis	130
Spleen	0·125–0·164	Chemical analysis	130
Brain, grey matter	0·21	Spectroscopy	136
Brain, white matter	0·10	Spectroscopy	136
Blood, whole	0·178±0·003	Spectroscopy	137
Blood, whole	0·184 (men)	Spectroscopy	138
Blood, whole	0·228 (women)	Spectroscopy	138
Blood, whole	0·216 (children)	Flame photometer	139
Blood, whole	0·600 (NaCl)	Chemical analysis	140
Blood, whole	0·615 (NaCl)	Chemical analysis	141
Blood, whole	0·635 (NaCl)		142
Blood, plasma	0·320(0·301–0·342)		143
Blood, plasma	0·322(0·317–0·327)	Flame photometer	58
Blood, plasma	0·324	Flame photometer	144
Blood, plasma	0·323		145
Blood, serum	0·335		146
Blood, serum	0·328		147
Blood, serum	0·320(0·315–0·350)		148
Blood, serum	0·324		149
Blood, serum	0·340(0·335–0·350)		150
Blood, serum	0·333		151
Blood, serum	0·325(0·289–0·378) (Indians)		152
Blood, serum	0·337 (Indians)		153
Blood, serum	0·319(0·308–0·329)	Flame photometer	154
Blood, serum	0·324 (mother)	Ionophoresis	155
Blood, serum	0·316 (child)	Ionophoresis	155
Blood serum	0·338(0·312–0·360) (Filipinos)		156
Blood, serum	0·328±0·0046		157
Blood, serum	0·329±0·002	Flame photometer	158
Blood, serum	0·305	Flame photometer	159
Blood, serum	0·303–0·375	Electrodialysis	160
Blood, erythrocytes	0·016–0·0276		161
Blood, erythrocytes	0·035–0·050		162
Blood, erythrocytes	0·097(0·037–0·130)		143
Blood, erythrocytes	0·041	Detd. directly	163
Blood, erythrocytes	0·036	Detd. indirectly	163
Blood, erythrocytes	0·038	Flame photometer	144

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TABLE III continued

Tissue	Sodium %	Method	Ref.
Cerebrospinal fluid	0·351		147
Cerebrospinal fluid	0·704–0·783 (NaCl)		164
Cerebrospinal fluid	0·295		149
Cerebrospinal fluid	0·725–0·800 (NaCl)		165
Cerebrospinal fluid	0·343	Pyroantimonate	166
Cerebrospinal fluid	0·335	Triple acetate	166
Cerebrospinal fluid	0·320–0·358		167
Serum exudate	0·303		142
Vesicular fluid	0·470–0·580		168
Eye, aqueous humor	0·409		159
Tears	0·823 (NaCl)		170–171
Gastric juice (fasting)	0·227		172
Gastric juice (fasting)	0·267(0·147–0·382)		173
Saliva	0·031–0·115		174
Saliva	0·0894±0·0022		175
Sweat	0·0110 (children)		176
Sweat	0·0276–0·182 At different seasons		177
Sweat	0·020–0·040		178
Sweat	0·0966 In Finnish Sauna bath		179

Slight differences in the sodium contents of plasma and erythrocytes are related to the sex and race of the blood donor.[145] Both plasma and lymph contain about 18 times as much sodium as potassium whereas the cellular tissues contain a relative excess of potassium.[195] Saliva secreted in response to stimulation contains higher concentrations of sodium and bicarbonate ions.[196,197] There is a definite diurnal variation in the sodium content of saliva although the potassium content remains fairly constant,[198,199] while both sodium and potassium concentrations gradually decrease with age.[200] The sodium content of tears is fairly constant, being independent of the rate of secretion,[201] but light increases the sodium content of ocular fluids.[202] The sodium content of gastric juice is related to the concentration of hydrochloric acid.[203,204]

There have been numerous attempts to correlate changes in the sodium contents of tissues with disease but the wide range of variation in normal individuals makes sodium determinations unreliable for diagnosis in the majority of cases. A definite change in the sodium content of blood serum has been demonstrated in patients suffering from anaphylactic shock,[205] pellagra and glossitis,[206] toxaemia,[207] congestive heart failure,[208] leukaemia and purpura,[209] diabetes and diabetic acidosis[210] and migraine.[211] Both the sodium–chloride ion ratio and the 'sodium space' are changed in cardiac conditions.[212,213] The sodium content of the cerebrospinal fluid is of little diagnostic value[214–216] except that it is increased in syphilitic patients.[217] The spinal fluid of patients suffering from general paresis influences the crystal habit of sodium chloride in a typical manner.[218]

(iv) Metabolism

There are a number of useful reviews of many topics of sodium metabolism including the general aspects,[219–224] water-salt equilibrium,[225–227] clearance of sodium chloride from tissue after injection[228] and the disturbances of sodium chloride metabolism in disease.[229-232]

The connexion between salt metabolism and the water balance of the body is complex, depending on the salt and water intakes, the ratios between ions, and the activity of the kidney and of the adrenals and pituitary glands.[233,234] A low intake of sodium chloride causes loss of water and of salt leading to low levels of sodium chloride in the blood; normal conditions are restored by simultaneous ingestion of salt and water. Excessive ingestion of salt and water, however, does not raise the sodium chloride level, while the ingestion of salt alone causes a water loss without loss of salt.[235] There is a certain minimum level of salt intake for retention of the normal body water. The ratio of the concentrations of sodium to chloride ions[236] and of sodium to calcium[237] in the blood also has an effect on the water balance. Excessive intake of water may lead to water intoxication with low sodium concentrations in the blood.[238,239] Administration of large amounts of common salt, orally or intravenously, causes a rise in the blood salt content and the blood volume is rapidly increased by the influx of water from the intercellular spaces;[240,241] some sodium also enters the cells.[242] The ingestion of ammonium chloride causes a sharp fall in the body sodium content leading to acidosis[243] while the calcium content of the blood is increased by injection of sodium bicarbonate.[244] Sodium chloride deficiency stimulates the adrenal cortex[245] and the cortical hormones conversely have an influence on the sodium level of the blood and on the permeability of tissues to sodium.[246,247] The blood sodium content is increased by stress or shock.[248] The carbon dioxide-binding capacity of the blood is greater in persons on a high salt diet owing to the higher serum sodium content.[249]

It is suggested that sodium is necessary for protein metabolism since a deficiency causes increased excretion of urea.[250] Ingestion of sodium chloride causes a sharp fall in the blood glucose content[251,252] while after intravenous injections of glucose the serum sodium content rises, indicating a possible connexion between sodium and carbohydrate metabolism.[253] Sodium chloride has been found to reduce excretion of glucose by diabetics.[254] There is also an increase in the respiration of tissues after a large salt intake.[255] The administration of sodium chloride to men doing hard muscular work has been found beneficial[256] in reducing fatigue and loss of weight.

There is an intimate relation between sodium and potassium metabolism. Thus the sodium content of the blood serum is increased both in potassium deficiency and in excess due to shifts in the ion distributions.[257,258] A high sodium chloride intake also results in a reduction of the body potassium.[259] The sodium-potassium ion ratio of gastric juice is 1:0·9 in normal and hyperacid cases and 4:1 in hypoacidity.[260] The standard free energy of exchange of sodium by potassium in connective tissue[261] is –1250g.-cal. at 37°C.

The availability of radioactive isotopes has stimulated a number of studies of the rates of exchange and of transport of sodium in tissues[262-272] and between mother and foetus.[273,274] The plasma half-life of sodium is approximately 6 days.[275-277] Only about 25% of the total sodium of human bone is exchangeable[277,278] as compared with 30–40% in rabbit and rat bone.[279-282] Sodium metabolism in the bones of dogs is drastically affected by adrenalectomy.[283]

Sodium chloride metabolism is disturbed in a number of diseases which have been summarised in a useful paper.[284] Primary disturbances include failure of endocrine control as in diabetes insipidus[285] or Addison's disease,[286] failure of kidney function or of the cell membrane permeability, while secondary disturbances include demineralisation from various causes or changes in the ionic balance of tissues. The oedema of starvation is also due to a disturbance of sodium metabolism.[287] Bacteria or substances that stimulate the reticuloendothelial system also stimulate sodium metabolism.[288] The ratio of chloride to sodium ions is altered in appendicitis or duodenal ulcer[289] and in Bright's disease.[290] The blood sodium content is changed in acidosis,[291] scurvy,[292] hyperthyroidism or hypertension,[293] pneumonia,[294] dystrophy[295] and acromegaly.[296]

(v) Sweat and Temperature Regulations

Considerable quantities of sodium chloride are lost through the skin by sweating, sometimes as much as 7g. in 2hr.[297-300] When sweating is avoided the loss is much reduced.[301] The concentration of sodium in the sweat increases with the temperature and is independent of the sweat rate.[302,303] There is little relationship between concentration and physical activity or condition of the subject.[304] In continuous sweating the concentration of sodium chloride tends to increase with time.[305] The chloride ion content of sweat depends on the intake[306] but decreases on acclimatisation to heat[307] and increases with the sweating rate.[308,309] Heat cramps and exhaustion are connected with salt loss and are relieved by ingestion of salt.[310,311] Tolerance to heat may be improved by simultaneous administration of salt and adrenal cortical hormone.[312] The electrolyte composition of sweat may in fact be used as an index of adrenal activity.[313] A study of the blood of a number of species suggests that the body temperature of vertebrates is determined largely by the salt content of serum and in particular by the sodium/potassium ion ratio.[314]

(vi) Excretion

The excretion of sodium and water is intimately connected with the maintenance of the correct balance of sodium in the body. Recently there have been considerable advances in our knowledge and understanding of the complex processes involved although there is still much that is obscure. Several excellent reviews and general articles are available.[315-318]

Sodium chloride is an excellent diuretic.[319] Ingested salt appears to be retained in the human body for long periods, only 25% being excreted within 3·5hr.,[320] while even smaller percentages are excreted in the same period by very young animals.[321] The dog appears to have a very efficient excretory mechanism, for large intakes of salt (up to 4g. per kg. daily) can be tolerated for many days without change of the blood serum content.[322] This should of course be taken into account when applying the results of animal experiments to human beings.

Urine is formed by the filtration of a fluid of approximately constant composition (blood plasma) in the glomeruli of the kidney followed by reabsorption of certain ions and molecules in different parts of the tubule of the kidney.[323] The cells of the proximal tubule of the frog are impermeable to sodium but permeable to potassium[324] while resorption of sodium and water takes place in the distal tubes. This resorption is controlled by hormones secreted by the adrenals. The increased output of urine caused by ingestion of salt is due to changes in the reabsorption of water rather than in the filtration rate.[325,326] A high velocity of fluid in the tubules would reduce the time of contact of the solution with the cells responsible for absorption and an increased excretion of sodium chloride would be expected.[327] The delay in resorption of sodium chloride in the tubules after ingestion of salt probably has a similar explanation.[328] The rate of excretion of sodium by human beings is not regarded as directly related to the glomerular filtration rate but this rate does have some influence since restriction of the circulation by means of compresses causes some reduction in the quantity of sodium excreted.[329] The volume of urine produced after injection of a saline solution is greater than the volume injected when this is administered slowly but less than this volume when the rate of injection exceeds a certain value.[330,331] The volume of urine may also depend on the volume of the extracellular fluid[332] and the distribution of fluid in the body does vary with the sodium chloride content.[333] Probably the resorption rate of sodium in the tubules depends both on the filtration rate and on a cation exchange process which may be independent.[334] The percentage of both chloride and nitrate ions escaping resorption rises with the concentration of the ions in the plasma.[335]

A hormone is secreted by the adrenal cortex which stimulates resorption of sodium and inhibits resorption of potassium.[336-339] Some progress has been made towards purifying this hormone.[340,341] Since about 97% of the sodium is resorbed, relatively small changes in the rate of resorption will control the balance of sodium in the body.[342] A reciprocal effect of salt on the output of the adrenals is suggested by the fact that immediately after the withdrawal of salt the concentration of 17-keto steroids falls off sharply in the urine, while that of the 11-deoxycorticosteroids increases, the concentration of other steroids falling more gradually.[343] The hormone appears to be produced in the *zona glomerulosa* of the adrenal cortex.[344] A similar hormone is responsible for controlling water balance and salt uptake in amphibians.[345,346] A microbioassay technique has been described for estimating such hormones.[347] Extracts of the posterior pituitary also have an effect on sodium excretion.[348,349]

Sodium excretion is greatly reduced in persons on a low salt diet.[350,351] The normal ratio of sodium to chloride ions is 0·92–1·10 but this increases greatly with large salt intakes.[352] The normal value, however, appears to be subject to very wide short term fluctuations,[353] and is reduced in certain diseases.[354] The rate of excretion of sodium ion is considerably increased when nitrate ion is also present in the body.[355] Ingestion of sodium bicarbonate causes increased excretion of sodium[356] in normal persons but sodium is retained in persons suffering from peptic ulcer.[357] The elimination of uric acid is suppressed on a high salt diet.[358]

There is a daily rhythm in the excretion of sodium.[359-361] The rate is also affected by breathing a carbon dioxide-rich atmosphere[362] and by posture, the rate of excretion being markedly reduced during quiet standing as compared with the supine position.[363,364] Bandaging the legs also reduces excretion because of the fall in renal plasma flow rate.[365,366]

A number of potent diuretics such as beer and alcohol,[367,368] p-carboxybenzenesulphonamide,[369] mersalyl,[370] thiomerin[371] and rennin[372] increase the excretion of sodium by reducing the resorption in the tubules. The diuretic effect of amphetamine may, however, be due to an increase in glomerular filtration rate.[372] Glycyrrhizic acid, the active principle of licorice, causes the retention of sodium.[374,375] Cationic exchange resins have recently been adopted as a treatment for reducing the body sodium content and preventing absorption in cases where this is desirable as a therapeutic measure. These resins are capable of absorbing 20–30mg. of sodium per g. during their passage through the intestine.[376-379] No ill effects result from feeding resins in amounts up to 5–10% of the diet.[380] The high rate of water excretion in diabetes insipidus results in increased elimination of sodium chloride,[381] while the increased retention of sodium in cardiac cases is attributed to a reduced glomerular filtration rate.[382,383] A similar retention is observed in pernicious anaemia.[384] In dropsy there is an increased ratio of sodium to chloride in the urine.[385] The danger of sodium depletion is the reduced excretion of urea which may result in uraemia.[386]

(vii) Specific Biological Effects

(a) Whole Organisms

Sodium chloride is fairly widely used in medicine and veterinary practice.[387,388] Intravenous injection of isotonic solutions causes a significant reduction of mortality from traumatic shock[389-391] and from toxaemia due to intestinal obstruction.[392] Sodium chloride is connected with the production of hypertension since a high salt intake leads to an increase of blood pressure in both man and animals.[393-396] Presumably the salt intake must exceed some minimum level which may be drastically lowered in certain abnormal physiological states, necessitating careful control of the salt intake.[397] Both sodium and chloride ions appear to be necessary for the production of hypertension.[398] The well-known production of thirst by ingestion of salt is not correlated with sodium or chloride ion concentrations in the blood[399,400] but is associated with a reduction in salivary flow.[401] Thirst can be completely inhibited by the intravenous injection of water slightly in excess of the volume which would normally have been drunk shortly before the adminstration of salt.[402]

Injection of hypertonic sodium chloride solutions increases the alkali reserve and the carbon dioxide content of the blood, whereas hypertonic solutions reduce the reserve.[403] Sodium salts are effective anticoagulants for blood, preventing the clumping of cells, and have been used successfully in blood transfusions.[404-408] Repeated injection of sodium chloride restores a low antibody-forming capacity of the blood to normal.[409] Both sodium chloride and sodium carbonate are useful in preventing anaphylactic shock after injection of sera.[410,411] Sodium halides stimulate the production of intestinal lymph.[412] Injections of sodium chloride cause a marked reduction of the pressure of the cerebrospinal fluid.[413] Sodium salts are also an important factor in the production of oedema in cardiac cases.[414,415] An excessive intake of common salt stimulates the thyroid causing an increase in the metabolic rate and a decrease in the ascorbic acid content of the blood.[416,417] The glucose tolerance of diabetic rats is restored to normal by sodium chloride[418] and the absorption of glucose in the intestine of dogs is accelerated.[419] Sodium bicarbonate increases the mobilisation of liver glycogen in rats possibly as a defence mechanism against the alkalosis produced.[420] Intravenous injection of sodium chloride is an effective antidote to poisoning by narcotics such as methanol, ethanol or chloral hydrate,[421] while sodium carbonate reduces fatalities from chloroform poisoning.[422] Low concentrations of sodium chloride stimulate the spermatozoids of frogs and toads[423] but higher concentrations reduce the motility of these and of human spermatozoa.[424] Degenerative changes are also found to occur in the testicular tissue of mice on a low salt diet.[425] Differences in the crystal form of sodium chloride are found when sera from normal and sarcomatous fowls are evaporated to dryness.[426] Administration of sodium sulphate reduces both the secretion and the solid content of bile in dogs.[427] Excess of common salt or of sodium sulphate in the diet leads to polyneuritis in pigeons.[428]

(b) Muscle

In muscle, as in certain other specialized tissues, there is a higher concentration of potassium ions than of sodium inside the cells. The most widely accepted theory is that the muscle cell membrane is freely permeable to ions, that the high internal concentration of potassium ions is maintained by means of an electrochemical gradient, and that sodium, although it can freely enter the cell, is actively transported outwards by a sodium extrusion mechanism (the so-called 'sodium pump').[429] Such a mechanism requires the expenditure of energy and the process has been shown to be linked to carbohydrate metabolism, being inhibited by typical inhibitors of metabolism.[430,431] Redistribution of the ions takes place when the muscle is transferred to a solution with a low potassium content but the original distribution is largely recovered on raising the potassium concentration of the solution.[432,433] The ionic content and also the water content of muscle are thus dependent on the composition of the blood serum in contact with the muscle.[434,435] Accumulation of potassium inside muscle is dependent on the outward flow of sodium ions,[436-438] but the outward flow of sodium ions appears to be independent of the external sodium concentration and does depend on the internal sodium and external potassium concentrations. The kinetics of the outward sodium transport have been studied but it is unfortunately difficult to compare the results obtained by different investigators since different muscles have been used and the conditions varied. The rate of outward transport has been estimated as 40 millimoles kg.$^{-1}$hr.$^{-1}$ and 10 micromoles cm.$^{-2}$sec.$^{-1}$ for the frog sartorius[436,438] and 28×10^{-12} equivalents cm.$^{-2}$sec.$^{-1}$ for the rat diaphragm.[440] The half times for the two muscles respectively are 30min.[436] and 10min.[440] In the frog sartorius the self diffusion coefficient of sodium ions in the extracellular fluid[438] is $3{\cdot}1 \times 10^{-6}$cm.^{2}sec.$^{-1}$, the transport requiring 0·1–0·5 of the energy of resting metabolism.[436,439] The temperature coefficient[436] is between 3 and 4. The velocity constant of ion exchange calculated as a 2nd. order reaction[441] is $1{\cdot}68 \times 10^{-3}$. The extracellular space calculated from the kinetics of release of radioactive sodium agrees reasonably well with that calculated by other methods.[442] The ratios of the permeability coefficients of potassium, sodium and chloride ions is $P_K:P_{Na}:P_{Cl} = 1:0{\cdot}027:0{\cdot}23$ and the membrane potentials calculated from these ratios agree well with measured potentials.[443] The influence of sodium concentration on the membrane potentials has been measured[444–446] and about one third of the potential may be attributed to the action of a 'sodium pump'. Ion exchanges probably occur during muscle contraction but the extent has not been accurately measured. Both contraction and the excitability depend on the ionic composition of the extracellular fluid,[447–456] in particular on the ratios of sodium, potassium and calcium ions. The chronaxia of frog muscle is increased by adrenal cortex extracts, probably through their action on the extracellular sodium.[457] Sodium chloride causes polymerization of muscle actin[458] and denaturation of myosin.[459–461] Contractions do not occur in frog muscle in Ringer solution containing less than 0·01N-sodium hydroxide but increase to a maximum at 0·04N.[462]

Over a certain range of concentrations sodium ions stimulate the rate of heart beat of frogs, at higher concentrations the rate is reduced.[463–470] A similar stimulation and inhibition occurs with intestine[471–477] and stomach. The actual sodium content of muscle varies with the species,[478] with the season of the year,[479,480] in different muscles of the same species[481,482] and during growth.[483] A small fraction of the sodium present in muscle appears to be bound and not freely diffusible.[484–486] The rate of clearance of sodium salts injected into muscle follows an exponential curve, and is related to the blood flow when this is between certain limits.[487-491] The sodium content of muscle is affected by respiratory acidosis,[492] injury,[493] fatigue,[494] the amount of salt in the diet[495] and the condition of the adrenals.[496] The normal sodium to chloride ratio is higher (2·27) than in plasma (1·35) in frogs.[497]

(c) Nerve Conduction

The role of cations in the conduction of nerve impulses has recently been reviewed.[498,501] Normally there is a higher concentration of potassium than of sodium inside the nerve axon. When an impulse passes along the axon the membrane becomes depolarised and specifically permeable to sodium ions which enter the axon, reducing the membrane potential and finally reversing it. The permeability of the membrane to sodium then becomes reduced and that to potassium increased, so that potassium ions now leave the axon until the potential is restored to its former resting value. The excess sodium inside the axon is now actively transported out by the 'sodium pump' mechanism and potassium re-enters until the original state is restored.[502-504] This process of sodium extrusion requires energy which is derived from metabolism, the amount being about 0·1 of the resting level.[499] The ionic contents of the giant axons of *Sepia officinalis* in the resting state are sodium 40 and potassium 325 millimoles per kg. During stimulation sodium enters at the rate of[505]

$3{\cdot}8 \times 10^{-12}$ moles cm.$^{-2}$ impulse^{-1}. Kinetic studies indicate that the nerve sheath is the barrier controlling the movement of ions,[506] but there is evidence that the loss of sodium occurs in two stages, a fast one depending on the nerve sheath and a slow one depending on the core. The diffusion coefficient of the core is estimated to be only 0·003 of the coefficient for free diffusion in aqueous solution.[507,508] The rate of diffusion of sodium into ganglia is estimated to be 0·02 times that in free solution.[509] The rate of loss of sodium from cat nerves is $3{\cdot}9 \times 10^{-12}$ mole cm.$^{-2}$sec.$^{-1}$ but is 100-5000 times as great in the region of the nodes of Ranvier.[510] The ability of the nerve to conduct is lost if the sodium concentration of the surrounding solution is lowered but can be restored by raising the concentration.[511-517] Lithium ions but not ammonium ions can replace sodium at least partially.[518,519] The nerve membrane is more permeable to cations than to anions at pH 7·4 but the permeability to anions increases as the pH is reduced.[520] Sodium extrusion is adversely affected by many factors which affect metabolism such as low temperature, anoxia, enzyme inhibitors etc.[521-525] Certain quaternary ammonium ions are even more effective than sodium in inhibiting the depolarization caused by potassium.[526] Sensitivity to excitation by acetylcholine does not appear to be connected with conduction but is likewise abolished by lack of sodium.[527] Sustained spontaneous discharges are set up in frog skin immersed in sodium chloride solution within a definite concentration range.[520] Injury to nerve causes a migration of sodium into the cut end and a loss of potassium through the surface.[529] In the spinal nerves of the bull frog, there is a gradient of sensitivity to lack of sodium along the length of the nerve.[530] Reducing the external concentration of sodium lowers the spike potential and membrane resistance.[531-535]

In the whole animal the production of tetany appears to be dependent on the sodium–calcium ratio in the blood serum.[536-538] An axon reflex sweat response is obtained after injection of sodium chloride solution and it has been proved that sodium ions must be present round the axon for a reflex response to occur.[539,540] There is a loss of sodium from nerve cells after only two days starvation.[541] The sodium and potassium contents of the nerves of the toad show variation with the season and also with temperature.[542] Many nerve blocking drugs act by interfering with the normal function of sodium.[543-545]

(d) Active Transport

Some aspects of active transport have already been discussed under Muscle (refs. 429–440) and under Nerve Conduction (refs. 498–505). Active transport may be defined as the transport of substances across a cell membrane which is influenced not only by the forces responsible for passive diffusion but also by other forces which are maintained and regulated by the metabolism of the cell.[546] A kinetic analysis of the problem suggests that mobility differences or electrostatic barriers alone cannot be responsible for the selective accumulation of ions.[547] Studies with radioactive isotopes indicate that the cell membrane of many cells which accumulate potassium is equally permeable to sodium and potassium.[548] The general acceptance of the concept of a sodium extrusion mechanism (the sodium pump)[429] has stimulated the search for a specific chemical substance or reaction chain capable of actively and selectively forcing sodium out of the cell. Suggestions include histamine[549] and the complex ions formed by sodium or potassium and adenosine triphosphoric acid and other polyphosphoric acids[550,551] but more evidence is available in favour of an oxidation-reduction pump theory[552-554] in which sodium ions are carried out of the cell attached to a respiratory metal catalyst in the reduced state. This mechanism may operate in yeast but not necessarily in all cells. The cytochrome-cyctochrome oxidase system appears to be associated with sodium transport through the eye lens.[555] Kidney mitochondria also actively

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transport sodium and potassium.[556-560] Transport requires only about 6% of the available metabolic energy during aerobic respiration but under anaerobic conditions it is estimated that 190–2500% of the energy would be needed depending on the temperature.[558] Radioactive tracer studies indicate that sodium exchanges in two fractions, one with a rapid, the other a slow turnover rate.[559] Adenine 5′-phosphate is necessary for maintaining ionic concentration gradients.[560] An uneven distribution of ions is observed in kidney-cortex slices in the absence of metabolic energy supplies suggesting that an ion exchange mechanism may operate since the cation distribution appears to rule out the Donnan effect.[561]

Although erythrocytes maintain a higher internal concentration of potassium than of sodium it is only a little over a decade since active transport has been conclusively demonstrated in this cell. Recent work has been well reviewed.[562] The connection between ion distributions and metabolism is now well established[563-566] although the dialysis of haemoglobin against Ringer solution has been shown to result in an accumulation of more potassium than sodium in the haemoglobin.[567] The average inward sodium flux is 3·08 ± 0·57meq./l. cells/hr. and the activation energies are 20,000 ± 2,700g.-cal./mole for the inward and 14,900 ± 3,400g.-cal./mole for outward transport.[568] The maintenance of the ion distribution requires a maximum of one third of the available glycolytic energy.[569] Although evidence from kinetics suggests that a single mechanism is responsible for active sodium transport and potassium accumulation,[570] lithium is found to compete with sodium but not with potassium while rubidium competes with potassium but not with sodium for transport, which suggests that there may be two different mechanisms involved.[571] Red cells have maintained a steady value for the outward flow of sodium for many months when stored under suitable conditions.[572] On cooling red blood cells to 2°C. some internal potassium is replaced by sodium but the original distribution is restored on returning the cells to 37°C.[573] Iodoacetate inhibited the outward transport of sodium but had no effect on inward flow, so that the cells gained 1·18meq. of sodium per litre, while there was a net loss of potassium of 1·80meq. per litre due to an increase in output and a decrease in intake.[574] The ratio of the concentrations of sodium in red cells and plasma differs in different groups of animals, sheep, ox, cat and dog having a higher ratio than man, baboon, rat and horse.[575]

Isolated frog skin actively transports sodium, accumulating it inside the skin, by means of a 'sodium pump', which requires phosphate-bond energy. A fraction of the sodium ions appears to penetrate by passive diffusion.[576,578] Lithium competes with sodium for transport.[579,580] The transport of sodium depends partially on the presence of potassium ions in the external solution which can be substituted by rubidium but not by ammonium ions which inhibit the transport.[581] Frog skin with Ringer solutions of the same concentration on each side has an active sodium transport potential of 75mV. This potential varies with the concentration of the solution outside the skin and the highest transport potential which has been measured is 138mV. as against the estimated potential of the 'sodium pump' of 150–170mV. The skin can produce a current of 19microamp. $cm.^{-1}$ due to the ion flux. The energy required for transport is only 3–5% of the available metabolic energy but the quantity of electricity transferred with the sodium ions is 70–90% of the electricity transferred by electrons in the oxidation process, indicating a very high efficiency for the pump. An oxidation reduction pump may be involved.[582] Sodium is transported faster than chloride ion while potassium is not taken up unless the skin potential is less than 30–40mV.[583] The potential difference across the skin is increased without effect on the rate of sodium transport by certain adrenal and pituitary hormones.[584] Many metabolic inhibitors and drugs inhibit active transport of sodium.[585,586] Active transport of sodium

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also occurs in the frog heart, in the chorion of the hen's egg[587] and in the malpighian tubules of insects.[588] Inhibitors of sodium transport include deoxycorticosterone,[589-591] cardiac glucosides,[592] cholinesterase inhibitors,[593-596] succinic dehydrogenase inhibitors[597] and carbonic anhydrase inhibitors.[598,599]

(e) Permeability of Tissues

The passage of molecules through the walls of capillaries occurs by the process of diffusion and the rate of diffusion of sodium chloride through the walls is 40 times the rate at which the salt is supplied to the tissues by the blood stream.[600,601] Anuria reduces the uptake of sodium through the skin in frogs;[602] the permeability is also decreased by astringents.[603] The ionophoretic transference number of sodium ions through living skin is 0·48 ± 0·03, independent of the source of the skin.[604] The rate of penetration of sodium ions through skin is increased by injection of deoxycorticosterone into the animal[605] and by hyaluronidase.[606] Penetration of sodium chloride through the skin into human beings becomes appreciable only when the applied concentration exceeds 10%.[607] The permeability of the heart to sodium ions appears to depend on acetylcholine metabolism.[608,609] The permeability to sodium chloride varies in different regions of the intestine and the rate depends on the salt concentration and on the pH of the blood.[610-613] Radioactive sodium has been used to study the penetration through cerebral tissue and into the aqueous humor,[614,615] through the lung[616] and from maternal blood to amniotic fluid.[617] The Donnan equilibrium does not apply to the barrier between the blood and the aqueous humor.[618,619] The rabbit cornea is less permeable to sodium than to potassium and relatively impermeable to chloride ions.[620] There is some evidence that sodium is actively secreted from the cornea into the aqueous humor.[621] The permeability of the cornea is increased in lenses with cataract caused by radiation.[622]

(f) Proteins

Calf thymus deoxypentose nucleic acid in sodium chloride solution binds per 4 atoms of phosphorus 2·28 atoms of sodium and 0·32 atoms of chlorine.[623] Deoxyribonucleohistone appears to dissociate into smaller fragments in sodium chloride solution.[624,625] The precipitation of antibodies by antigens is markedly dependent on the sodium chloride content of the solution although no binding of the ions by the precipitate can be demonstrated.[626-629]

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Effect on Enzymes

Sodium ions have a marked effect on many enzyme systems, either stimulating or inhibiting the reactions. In some cases this effect is a simple salt effect but in others it appears to be specific since potassium and sodium often have opposite effects. Sodium has an inhibitory effect on anaerobic glycolysis and more than one step may be affected. The effects of potassium and sodium are opposed. Sodium retards glycogen formation and stimulates its breakdown, possibly by acting on phosphorylase. The transfer of phosphate from phosphoenolpyruvate is also inhibited.[1-5] The respiration of a suspension of brain tissue is stimulated[6] but that of kidney tissue reduced[7] by sodium ions. Low concentrations of sodium ions stimulate the oxidation of citrate by kidney mitochondria whereas higher concentrations inhibit this reaction.[8] The ability of rat liver to transfer methyl groups from methionine to nicotinamide appears to require a minimum level of sodium chloride.[9]

The action of sodium on specific enzyme systems is given in Table IV.

Refs. p. 1448

TABLE IV.- EFFECT OF SODIUM ON ENZYMES

Enzyme	Source	Effect	Ref.
Acetate activating	-	-	10
Alcohol dehydrogenase	Yeast	-	11
Amylase	-	+	12
Amylase	Bacterial	+	13
Amylase	Fowl stomach	++	14
Amylase	Pancreas	++	15,16
Amylase	Saliva	++	17,20
Aspartic deaminase	*V. cholerae*	Stab.	21
Carbonic anhydrase	Spinach	Stab.	22
Carboxypeptidase	-	+	23
Catalase	Blood	-	24-26
Cholinesterase	-	+	27
Cytochrome oxidase	-	+	28
Cytochrome oxidase	Bacterial	+	29
Cytochrome oxidase	Mouse melanoma	+	30,31
Diastase	Malt	-	32
Deoxyribonuclease	-	+	33
Formic dehydrogenase	Bacterial	-	34
Lactic dehydrogenase	Bacterial	-	35
Lipase	Pancreas	+	36
Lysozyme	Egg white	+	37-39
Mucinolytic	-	+	40
Myokinase	-	--	41
Pantothenate synthesising	Bacterial	-	42
Pectinase	-	++	43
Pectin glycosidase	-	-	43
Pectin esterase	-	-	44
Pepsin	-	-	45,46
Peroxidase	-	-	47
Phosphoglucomutase	*Phaseolus r.*	-	48
Ptyalin	Saliva	+	49
Pyruvate phosphoferase	Erythrocytes	-	50
Rhodanese	Liver	-	51
Tryptophanase	Bacterial	-	52
Urease	-	-	53,54

++ Marked stimulation
+ Stimulation
- Inhibition
Stab. Stabilizes

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